THE MASSACHUSETTS
TOXICS USE REDUCTION INSTITUTE

THE USE OF AN ULTRAFILTRATION UNIT IN A CLOSED LOOP AQUEOUS CLEANING SYSTEM

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The Use of an Ultrafiltration Unit in a Closed Loop Aqueous Cleaning System
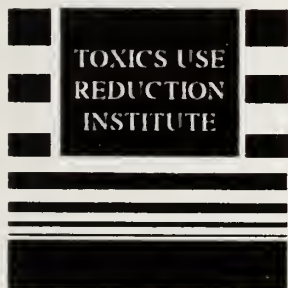
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Toxics Use Reduction Institute
Research Fellows Program

In 1991, the Toxics Use Reduction Institute established the Research Fellows Program at the University of Massachusetts Lowell (UML). The Research Fellows Program funds toxics use reduction projects performed by a graduate student and his/her advisor. The goals of the Research Fellows Program are:

- to develop technologies, materials, processes, and methods for implementing toxics use reduction techniques
- to develop an understanding of toxics use reduction among UML graduate students and faculty
- to facilitate the integration of the concept of toxics use reduction into UML research projects
- to provide UML faculty with "incubator" funding for toxics use reduction related research, and
- to act as a liaison between Massachusetts industries and UML faculty.

Notice

Abstract

The intent of this research was to evaluate the potential of ultrafiltration (UF) to successfully "close the loop" for different aqueous cleaning applications. The evaluation was based on data obtained from experimental work in which a variety of cleaner/contaminant test solutions were processed through three membranes of different types and pore sizes. This project also included researching and reporting on aqueous cleaner compositions and contaminants commonly encountered in aqueous cleaning. A qualitative evaluation of the recyclability of different cleaner/contaminant solutions based on oil-surfactant tradeoff was performed. The research implied that any of the three membranes studied is capable of successfully recycling aqueous cleaning baths containing hydrocarbon oil-based contaminants. However, UF did not appear to be well-suited for recycling aqueous cleaning baths containing synthetic contaminants. In addition, the research further validated equations developed to describe flux and flux decline in UF.

Acknowledgements

Table of Contents

iv

List of Tables

List of Figures

viii

I. INTRODUCTION

1.1 Project Purpose

Traditionally, metal parts and electronic components were cleaned with chlorinated solvents. However, concern over the depletion of the ozone layer has led to a phase-out in the production of some of these solvents, while the use of others is being curtailed or eliminated due to adverse health effects [Lorincz, 1993; Quitmeyer, 1991]. In an effort to efficiently clean parts and assemblies without the use of chlorinated solvents, companies are turning to aqueous cleaning. Membrane filtration techniques to "close loop" the aqueous cleaning processes are being used to make these processes even more economical and environmentally friendly. Such membrane filtration techniques include ultrafiltration.

This research project involved the study of the use of ultrafiltration in closed loop aqueous cleaning systems. The intention of this research was to evaluate the potential of ultrafiltration to successfully "close the loop" for different aqueous cleaning applications. The evaluation was based on data obtained from experimental work which consisted of processing a variety of cleaner/contaminant test solutions through membranes of different types and pore sizes. In addition, this project included researching and reporting on aqueous cleaner compositions and contaminants commonly encountered in aqueous cleaning, as well as a qualitative evaluation of the recyclability of different cleaner/contaminant solutions based on oil-surfactant tradeoff.

1.2 Environmental Impacts and Toxics Use Reduction Implications

As stated, the vast majority of both metals and electronics parts cleaning was historically performed using chlorinated and fluorinated hydrocarbons. Again, it was concern over the depletion of the ozone layer that prompted the passage of international treaties and the development of regulatory measures calling for a freeze and eventual phase-out of the production of many chlorinated solvents, including CFCs, 1,1,1-trichloroethane, and carbon tetrachloride [Evanoff, 1994]. In addition, toxicity effects associated with solvents such as methylene chloride, perchloroethylene (PCE or perc), and trichloroethylene (TCE) have caused concern over their use [Quitmeyer, 1991].

In response to these environmental and health concerns, industry looked to alternative cleaning methods. As suggested, a technology which could substantially replace the use of chlorinated solvents is aqueous cleaning. Aqueous cleaning combines a water-based cleaning solution and some type of mechanical cleaning action. In particular, alkaline cleaners are viewed as the most viable substitute for chlorinated solvents. However, without a recovery and reuse system, an alkaline cleaning bath is disposed of at fairly rapid rates, resulting in the production of large volumes of potentially hazardous wastewater. The use of membrane filtration to "close the loop" on aqueous cleaning can significantly reduce waste volumes by both concentrating the sludge accumulated in the cleaning process and extending the life of the cleaner bath by an average of seven to ten times. Extension of bath life also translates into a reduction in the amount of cleaning chemicals which must be utilized.

1.3 Potential Commercial Applications

Closed loop aqueous cleaning is a proven technology which can increase process efficiency and decrease the generation of waste [Fuhrman, 1995]. Closed loop systems range in capacity from 50 gpd to over 100,000 gpd and are designed to retrofit into currently operating aqueous cleaning systems. With a membrane filtration unit, cleaning waste disposal costs are minimized, as are the annual operating costs associated with aqueous cleaning. Currently, the greatest implementation barrier for closed loop systems are economic factors. Many small and mid-sized firms cannot afford the capital expenditures associated with the selection, purchase, and start-up of a closed loop system. This research was designed as an effort to eliminate a portion of the guess work associated with the selection of a closed loop system. Based on conclusions drawn from this research, firms would be able to narrow their choices based on the type of cleaner/contaminant system they are using.

1.4 Aqueous Cleaners

Components of alkaline aqueous cleaners may be divided into three general categories: surfactants, builders, and additives. Surfactants are molecules which are preferentially absorbed at water-hydrocarbon interfaces. They are comprised of both a hydrophilic (water-soluble) and a lipophilic (oil-soluble) group and may be classified as anionic or nonionic depending upon the charge of the hydrophilic group. Surfactant properties include wetting, solubilizing, emulsifying, dispersing, foaming, and anti-foaming. Builders are inorganic alkaline salts which enhance the effects of the

surfactants. Their functions may include saponification of fatty soils, control of water hardness and other ions, deflocculation of contaminants, and maintenance of cleaner alkalinity by providing both reserve alkalinity and buffering. Different types of builders include phosphates, carbonates, hydroxides, zeolites, and silicates, which also inhibit corrosion of ferrous substrates. Additives, which may overlap builders in function, act primarily as contaminant dispersants, water softening agents, detergent fillers, and corrosion inhibitors. Examples include amine compounds and various polymers.

1.5 Aqueous Cleaning Mechanisms

As stated, surfactants are molecules comprised of both a hydrophilic (water-soluble) and a lipophilic (oil-soluble) group. The unique chemical nature of surfactants allows them to be preferentially absorbed at water-hydrocarbon interfaces, causing the lowering of interfacial tensions between water and hydrocarbon-based contaminants. It is by this lowering of interfacial tensions that surfactants are able to solubilize contaminants [Toxics Use Reduction Institute and Biodegradable Polymer Research Center, 1996].

When surfactants are added to an aqueous solution in sufficient amounts, the majority of the surfactant molecules form aggregates known as micelles. These micelles are often spherical in shape, with all of the hydrophilic ends of the surfactant oriented outward toward the bulk aqueous solution. The micelles are the structures which effect the solubilization and emulsification of hydrocarbon-based contaminants. The actual solubilization mechanism is best described in five steps (see Figure 1) [Toxics Use Reduction Institute and Biodegradable Polymer Research Center, 1996]

1. The micelle diffuses to the surface of the contaminant.

2. The micelle is adsorbed at the contaminant-water interface.

3. Contaminant molecules mix with the adsorbed surfactant molecules.

4. The surfactant micelle is desorbed from the contaminant surface.

5. The micelle containing solubilized contaminant diffuses into the bulk of the

water.
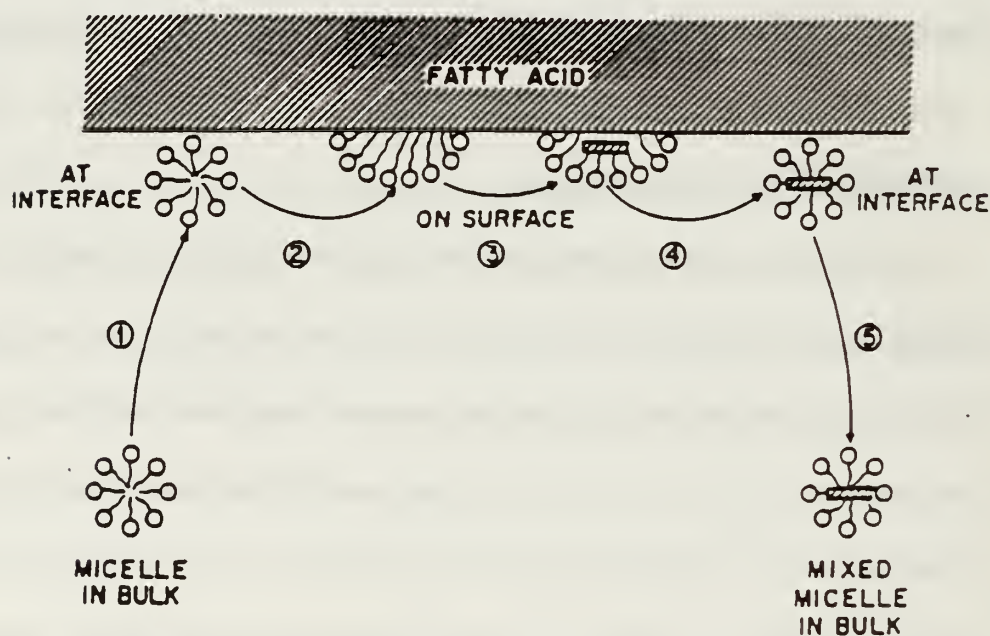
Figure 1. Solubilization and Emulsification of Oil by a Micelle

1.6 Contaminants

Typical contaminants encountered in metals and electronics cleaning are listed in Table 1 [McLaughlin, 1995]. Particularly of interest are the hydrocarbon oils, waxes, and greases used for purposes such as lubrication, corrosion inhibition, and cooling during machining processes. These hydrocarbon compounds may exist either in an emulsion within the cleaning solution due to the presence of surfactants, or as a separate phase.

When present as a separate phase, the hydrocarbons can typically be removed simply by skimming. However, if the hydrocarbon phase is emulsified or becomes temporarily dispersed within the cleaning solution through mechanical means, the hydrocarbons can only be removed by more elaborate means (e.g., ultrafiltration).

Table 1. Common Contaminants of Metal and Electronic Parts

Metal Parts	Electronic Parts
hydrocarbon oils	resins
hydrocarbon waxes	rosins
hydrocarbon greases	fluxes
silicone oils	conductive residues
organic solvents	particulates
buffing compounds	salts
mold-release agents	
metallic complexes	
metal oxides	
trace metals	
particulates	
scale	
salts	

Lubricants in particular may be divided into five major classifications: mineral oils, natural oils, emulsions, semi-synthetics, and synthetics. Mineral oils are paraffinic and naphthenic hydrocarbons used primarily for lubrication purposes. Natural oils are of vegetable or animal origin and are also used primarily for lubrication purposes. Emulsions (or "soluble oils") are formulated oil mixtures typically containing a naphthenic mineral oil base along with emulsifiers and other additives. This mixture is combined with water to create an oil-in-water emulsion. Emulsions combine the lubrication properties of oils with the cooling properties of water. Semi-synthetics are microemulsions containing water, mineral oils, emulsifiers, dispersants, and other

additives. They are primarily used as machining coolants. Synthetics contain no oils and are typically composed of polyglycol, polyisobutylene, and poly alpha-olefin bases. These are also primarily used as machining coolants

1.7 General Description of Ultrafiltration

A membrane is a physical barrier between two fluids, which, in the case of ultrafiltration (UF), separates the components of the fluids based on their molecular size differences. Smaller particles pass through the porous UF membrane with the bulk flow of solvent (permeate), while larger particles are rejected and remain in the feed solution (retentate) (see Figure 2). UF uses a membrane with pore sizes ranging from approximately 0.001 to 0.2 microns. UF membrane pore sizes are also specified by molecular weight cut-offs (MWCOs). The MWCOs for UF membranes typically range from 300 to 500,000 daltons, and are defined by the smallest molecular weight species which has 90% rejection. UF is a pressure-driven process, with typical pressure drops across the membrane ranging from 10 to 100 psig [Wankat, 1994]. Such pressures are required to overcome the low to moderate osmotic pressures incurred during UF.

Note that microfiltration (MF) is also used in closed loop systems. MF and UF are differentiated by membrane pore size. MF membrane pore sizes range from approximately 0.05 to 2.0 microns [Osmonics, Inc., 1996]. Many of the membranes used for closed loop cleaning have pore sizes in the 0.05 to 0.2 micron range, where differentiation between MF and UF becomes largely a matter of membrane manufacturer preference.

UF is suitable for use in a closed loop cleaning system for two major reasons. First, experimental results indicate that the proper selection of membrane pore size for a particular cleaning chemistry can selectively remove bath contaminants (i.e., emulsified oil and other relatively large molecules), while simultaneously permitting the majority of the aqueous cleaner components (i.e., surfactants, builders, and additives) to pass through. Selection of the proper membrane pore size is reduced to a tradeoff between retention of emulsified oil and passage of cleaner components. Secondly, UF membrane modules utilize a crossflow configuration (see Figure 2) which splits the cleaner into an (almost) oil-free permeate stream and an oil-rich retentate stream. This permeate stream, which contains the cleaner components, can be recycled back to the aqueous cleaning bath for reuse. The oil-rich retentate stream is sent to a collection tank where the oils can be concentrated for disposal. The crossflow configuration maximizes flow capacity and minimizes membrane fouling, allowing for the processing of high volumetric flow rates of contaminated cleaner solution. For an excellent review of closed loop UF systems, refer to articles by Peterson (1995) and Evanson (1995).

In UF, the separation of different species is accomplished through sieving and depth filtration. Sieving is the dominant mechanism [Cherkasov, 1990] and refers to the exclusion of solute particles based on size. Depth filtration occurs when solute particles adhere to the membrane surface or become lodged within the porous structure. UF is performed in a crossflow configuration to produce tangential flow at the membrane surface which in turn creates shearing forces at the surface [Wankat, 1994; McCabe et al, 1993; Jonsson, 1990; Murkes, 1990]. These shearing forces slow and limit, but do not

prevent, the buildup of a gel layer at the membrane surface. Gel layers act as a resistance to filtration. They are the result of a phenomena known as concentration polarization, which occurs as rejected solute particles concentrate at the membrane surface. In the case of UF, these particles are relatively large and therefore exhibit low liquid diffusivities. Thus, they tend not to diffuse back into the bulk solution at a rate equal to the rate at which they are carried to the membrane by the flux of solvent. This difference in transport rates results in a concentration gradient (see Figure 3) which leads to the formation of a gel layer.
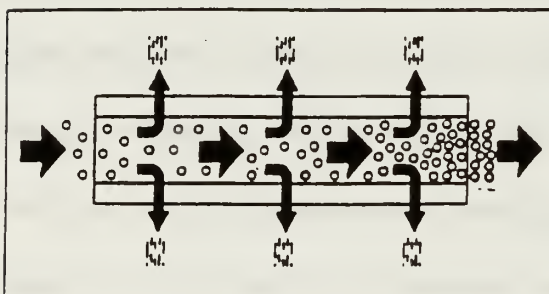
Figure 2. Crossflow Filtration
[Fairey Ind. Ceramics, Ltd, 1993]
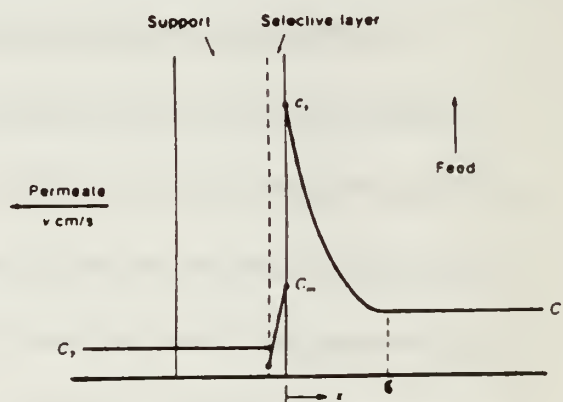
Figure 3. Concentration Gradients in
UF Membrane [McCabe et al, 1993]

Over time the membrane flux will decline from membrane fouling. Fouling may occur as a direct result of depth filtration, where particles become attached within the internal pore structure or surface of the membrane due to adsorption, precipitation, steric factors, adhesion, etc. Fouling may also occur from the formation and compaction of a stagnant gel layer on the membrane surface. These fouling mechanisms have been

explored and summarized by Muralidhara (1991) and Rolchigo (1991). However, as flux declines, the solute rejection often increases, leading to a superior separation over a limited time period [McCabe et al, 1993].

1.8 Theoretical Background of Ultrafiltration

Much research has been done to determine the expressions governing transport phenomena in UF [Henriksen and Hassager, 1993; Brites and de Pinho, 1991; Jonsson, 1990; Murkes, 1990; Eman, 1989]. The basic mass transfer equation describing UF [McCabe et al, 1993] states that the flux of the solute due to convection plus diffusion is constant in the boundary layer and equal to the flux of solute in the permeate (see Figure 3). The equation is as follows:

$$vc + D_v(dc/dx) = vc_2 \qquad (1)$$

where the volume flux, v, is the superficial permeate velocity normal to the membrane surface, c is the solute concentration on the feed side, D_v is the volumetric diffusivity of the solute, and c_2 is the concentration of solute in the permeate. Integrating with the boundary conditions $c=c_s$ at $x=0$ and $c=c_1$ at $x=\delta$ (the thickness of the concentration boundary layer) yields:

$$\ln[(c_s-c_2)/(c_1-c_2)] = v\delta/D_v \qquad (2)$$

Note that the quantity D_v/δ is defined as the mass-transfer coefficient k_c. Also, in cases of total solute rejection, $c_2=0$ and Eq. 2 simplifies accordingly.

The superficial permeate velocity, v, for a clean UF membrane may be determined from a modified Hagen-Poiseuille equation:

$$v = [(\Delta p - \Delta \pi)g_c D^2 \varepsilon]/[32 L \tau \mu] \qquad (3)$$

where Δp is the pressure driving force across the membrane, $\Delta \pi$ is the difference in osmotic pressures across the membrane, g_c is the Newton's-law proportionality factor, D is the average pore size, ε is the membrane void fraction, L is the nominal thickness of the active layer of the membrane, τ is a tortuosity factor, and μ is the viscosity of the membrane feed. It is difficult to get independent measurements of D, ε, L, and τ, but these characteristics are incorporated into the membrane permeability, Q_m, which is the flux of pure water at room temperature per unit pressure drop. For UF use, the superficial permeate velocity (or volume flux) for a clean membrane can be predicted from Q_m, the driving force $(\Delta p - \Delta \pi)$, the viscosity of pure water at room temperature (μ_{H2O}), and the viscosity of the permeate solution (μ):

$$v = Q_m(\Delta p - \Delta \pi)\mu_{H2O}/\mu \qquad (4)$$

By comparing the relationship between equations (3) and (4), the effects of changing membrane properties on membrane permeability can be determined. In

particular, increases in membrane pore size (D) and membrane void fraction (ε) will increase membrane permeability (Q_m), and vice versa. Further, increases in the thickness of the selective layer of the membrane (L) will decrease membrane permeability (Q_m), and vice versa.

In UF, the flux for a given membrane increases linearly with Δp at low Δp, but then levels off to a maximum limiting value independent of Δp at higher Δp. This limiting flux is the direct result of concentration polarization because, as flux increases, c_s also increases. The limiting flux occurs when c_s reaches the solubility limit of the solute (i.e., the concentration at which the gel layer begins to form). The limiting flux value can be increased by increasing the tangential feed flow velocity in the crossflow system. Increasing tangential velocity decreases δ, and it follows from Eq. 2 that the flux, v, must increase.

In the case of partial solute rejection (e.g., where a fraction of the membrane pores are larger than the solute to be removed), the fraction of solute rejected can be expressed as:

$$R = 1 - c_2/c_1 \qquad (5)$$

where the concentration values were defined earlier. The rejection, R, depends mainly on the ratio of the solute size to the pore size, λ, which determines the partition coefficient K, and on the ratio v/k_c [McCabe et al, 1993]. An expression for R when diffusion in the membrane is negligible and solute is carried through the pores by permeate flow follows:

$$(1-R)/R = [K/(1-K)]exp(v/k_c) \qquad (6)$$

where $K=(1-\lambda)^2$. Fell et al (1990) provide a comprehensive review of the factors affecting both flux and rejection.

1.9 Ultrafiltration Membrane Materials

Early UF membranes were predominately constructed from polymeric materials [Wankat, 1994]. Among the earliest polymeric materials were cellulose acetate and polypropylene (PP). However, as studies began to confirm that hydrophilic membranes were more resistant to fouling in the majority of UF applications [Jonsson, 1990; Bil'dyukevich, 1989], research was conducted into developing such membranes. Later developments included polyvinylidene fluoride (PVDF), polysulfone [Staude and Breitbach, 1991], polyvinyl chloride, and polyacrylonitrile (PAN) hydrophilic membranes. However, these membranes still were susceptible to rapid fouling and degradation (e.g., swelling and dissolution) when used with solvent-rich feeds. Taking this into account, more recent developments are polyaramide [Magerstadt et al. 1993] and polyphenylene sulfide sulfone [Kurihara, 1991] membranes, which combine hydrophilicity with solvent-resistance. However, the vast majority of polymeric membranes are still poorly suited for high temperature, extreme pH applications. This prompted industry to investigate inorganic membranes, which are durable and dependable at even the most extreme conditions, as an alternative. First to be developed were the

zirconia, titania, and alumina oxide ceramic membranes [Larbot et al, 1989]. An off-shoot of these ceramic membranes was ceramic-polymeric membrane hybrids, which are also known as dynamic membranes [Doyen et al, 1990; Townsend et al, 1989]. A further development along this same vein was the ceramic-metal mesh membranes, which consist of a metal mesh over which a ceramic slurry is dried [Cowieson, 1992]. Most recently, industry has begun developing carbon-graphite composite membranes, which consist of a pure carbon substrate coupled with a thin selective layer of carbon or ceramic. These composite membranes are comparable to the ceramic membranes in performance [Le Carbone, 1993].

Presently, the UF membranes most commonly used for closed loop aqueous cleaning are polymeric (polyvinylidene fluoride (PVDF), polypropylene (PP), and polyacrylonitrile (PAN)), ceramic (zirconia or alumina oxide), and carbon composite.

1.10 Membrane Fabrication

The structure of a membrane may be defined as symmetric (i.e., pore diameter constant over membrane cross section) or asymmetric (i.e., pore diameters increase from one side of the membrane to the other by a factor of 10 to 1000) [Strathmann, 1985]. In general, asymmetric membranes provide superior selectivity and mechanical stability over symmetric membranes. Polymeric membranes for UF are asymmetric and are prepared by a variety of methods [Munari et al, 1990]. One such method is phase inversion, where the polymer is first dissolved in an appropriate solvent and spread as a film (20 to 200 microns thick) on a support. A precipitating agent (or nonsolvent) is then added to the

film, resulting in two phases: a polymer-rich phase and a liquid solvent-rich phase. The resulting asymmetric membrane consists of a dense, very thin porous skin layer atop a very porous, thick substructure. Both layers are the same polymer, with the asymmetry resulting from more rapid precipitation at the film surface. The skin serves as the selective layer for the membrane, with the substructure providing support. As an alternative to the addition of a nonsolvent, phase separation of the polymer-solvent solution may be induced by thermal gelation (i.e., cooling the solution) or evaporation of the solvent from the solution. In addition, composite membranes may be formed by depositing a thin polymer film on a preformed substructure [Strathmann, 1985]. Ceramic and carbon-based membranes are considered more symmetric in pore shape, although they tend to have very irregular pore structures. These membranes are most commonly formed by sintering powders of the desired membrane material.

1.11 Membrane Characterization

The effectiveness of a membrane separation is directly evaluated through mass transport properties (i.e., transmembrane flux and solute rejection). These two factors represent the main membrane characterizing parameters. Unfortunately, for a given membrane, these parameters are often very case-specific and depend directly on the type of solvent and solute to be separated. However, flux and rejection are related to the pore density, diameter, and size distribution, and it follows that measuring these parameters is a method of characterizing a given membrane. Other important factors for membrane characterization include temperature stability, and chemical and mechanical resistance. A

variety of methods are currently used to evaluate membrane structure and transport properties, including microscopic observation, MWCO determination, porosity measurements [Abaticchio et al, 1990], gas adsorption and desorption measurements, permeability measurements, rejection and selective permeation measurements, the bubble pressure method, the liquid displacement method, mercury porosimetry, thermoporometry, and permporometry [Cuperus and Smolders, 1991]. An actual correlation of permeability and solute uptake has been developed by Rodgers et al (1995).

1.12 Membrane Configurations

Membranes are incorporated into modules to maximize the available membrane surface area for a given volume. In this way, the maximum permeate flow through the surface area of the membrane (or flux) is achieved. There are currently five basic module designs commonly used for UF (see Figure 4). The plate-and-frame module (Fig. 4B) has its origin in the conventional filter press concept and consists of membranes, porous membrane support plates, and spacers forming the feed flow channel clamped together and stacked between two end plates. The spiral-wound module (Fig. 4C) consists of a feed flow channel spacer, a membrane, and a porous membrane support rolled up and inserted into an outer tubular pressure shell. A tubular membrane module (Fig. 4D) consists of membrane tubes (with diameters ranging from 1 to 2.5 cm) placed in porous pipes (fiberglass or stainless steel) either by casting the membrane directly on the pipe wall or by preparing the membrane as a tube and inserting it into the pipe. The capillary membrane module (Fig. 4E) consists of a large number of membrane capillaries (with

inner diameter of 0.2 to 3 mm) arranged in parallel as a bundle in a shell tube. Lastly, the hollow fiber membrane module (Fig. 4F) consists of a bundle of several thousand membrane fibers in a half loop installed in a pressure shell, with the free ends fixed by an epoxy resin [Strathmann, 1985].

The most common configurations used in closed loop cleaning membrane modules are tubular, spiral wound, and hollow fiber. Ceramic and carbon composite membranes are limited to the tubular configuration. A typical closed loop cleaning system would incorporate a particulate filter and skimmer in conjunction with the membrane module to effectively recycle the cleaning solution.
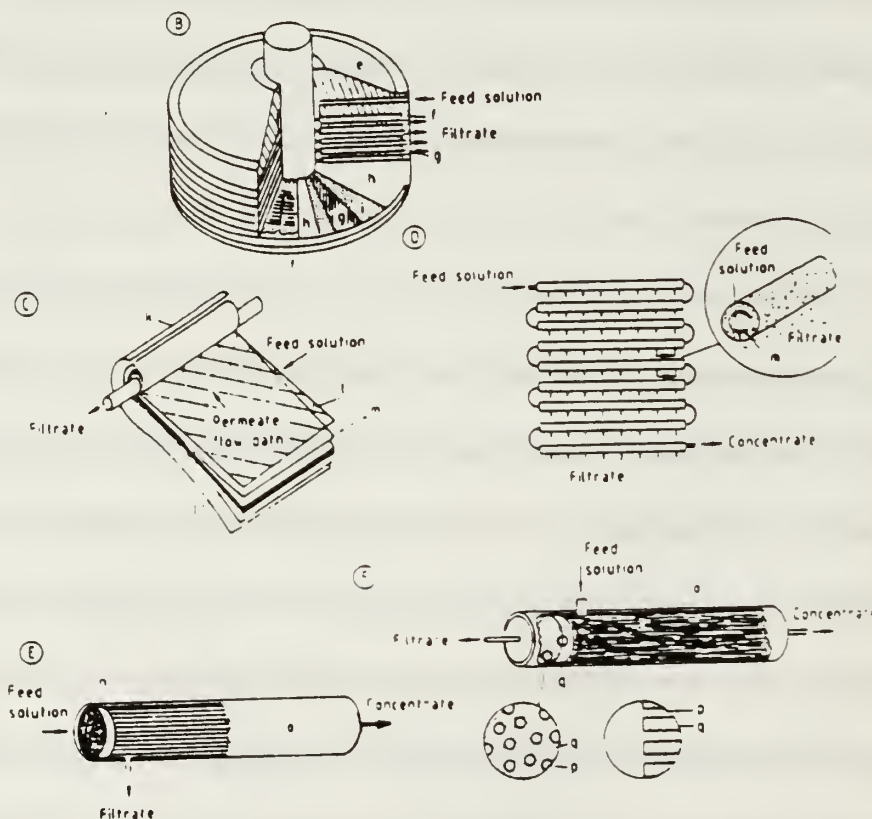
Figure 4. Membrane Modules Commonly Used in Ultrafiltration [Strathmann, 1985]

a) Filter cartridge; b) Knife-edge seal. c) Filter housing. d) Flat resilient gasket; e) End plate; f) Spacer; g) Membrane support plate; h) Membrane; i) Filter paper; j) Porous membrane support; k) Cover leaf; l) Spacer screen; m) Membrane n) Capillary membrane; o) Shell tube; p) Hollow fiber; q) Epoxy resin

1.13 Results of Literature Search

Aside from much of the background information presented in the previous sections, a literature survey indicated that there is significant amounts of work currently being conducted in the area of closed loop aqueous cleaning. Although the concept of using membrane filtration to extend cleaner life has existed since at least the late 1970's [Bailey, 1977], the idea never achieved large-scale use because the simplicity and effectiveness of vapor degreasing impeded the switch to aqueous cleaners, let alone closed loop aqueous systems. However, as recent legislative measures have prompted the switch to aqueous cleaning [Furhman, 1995], research into closed loop aqueous cleaning has increased.

The majority of the literature published in the early 1990's was aimed only at increasing industry awareness of this technology and provided little insight into the actual selection and operation of closed loop systems. During this time, the application of this technology was still in its infancy. This changed within the last few years, as literature documenting concrete selection and operating parameters has begun to appear [Carmody, 1995; Woodrow and Barnes, 1995]. However, because of the competitiveness associated with the development of this technology, few equipment manufacturers are willing to publish their findings.

In addition to technical literature, much has been published documenting the economic viability of closed loop aqueous cleaning (refer to Section 1.14 for specific case studies). Studies have suggested that the operating costs associated with aqueous cleaning systems are comparable to those of similar sized vapor degreasers. Although

closed loop cleaning systems are very application-specific, in many instances favorable payback periods on capital expenditures can be expected, as well as large savings on cleaner purchases and disposal costs.

Discussions with closed loop system manufacturers, including U.S. Filter Corp., Membrex, Inc., Koch Membrane Systems Inc., MSC Liquid Filtration Corp., and Infinitex Inc., have demonstrated the need for proper operation and maintenance, which is essential for prolonging the life of the membrane and the reliable, predictable operation of the closed loop system. Crossflow filtration techniques depend upon a high flow rate to maintain turbulent flow through the membrane module. Turbulent flow provides the agitation necessary to slow the rate of membrane fouling but does not prevent it. Thus, regular cleaning of the membrane is necessary. A typical cleaning process includes purging the system of all contaminated cleaner bath, circulating a cleaning solution, removing this solution and flushing with water, testing the flux using fresh water, and finally bringing the system back into operation.

Discussions with closed loop system manufacturers also suggest that the majority of filtration units currently produced are appropriate for use in practically any cleaning application. One exception to this is cleaning applications performed at high temperatures (>140 F) and pH levels(>11-12) [Peterson, 1995]. In such cases polymeric membranes may rapidly degrade, and ceramic or carbon composite membranes should be used. Also, certain applications using cleaners with high concentrations of silicates have been shown to prematurely end membrane life due to pore clogging by silicate-based precipitates [Meltzer, 1993]. In such cases, a switch to a non-silicated cleaner is often the

most feasible alternative. The effects of various contaminants on the recyclability of different cleaners and the effects of membrane pore size with respect to the oil-surfactant tradeoff remain undetermined.

Finally, discussions with cleaner manufacturers [Quitmeyer, 1995] have revealed that two proposed mechanisms exist to describe the recycling of surfactants in aqueous cleaners processed through closed loop UF systems. It is known that the majority of the surfactants in an aqueous cleaning bath that are not associated with "mixed micelles" will pass through the UF membrane because of the small molecular weights of the surfactant molecules (refer to Section 1.5 for a description of oil emulsification by surfactants). However, the question exists as to whether the surfactants associated with "mixed micelles" are stripped from the surface of the emulsified oil droplets when the "mixed micelles" contact the UF membrane. If this were the case, the majority of the surfactants would pass through the membrane while the oil droplets would be rejected. If, on the other hand, the "mixed micelle" remained intact (i.e., the surfactants are not stripped from the surface of the oil droplet), all of the surfactant required to emulsify the oil droplets would be retained by the UF membrane, and thus the amount of surfactant recycled through the membrane would decrease dramatically. Future research performed in the area of closed loop aqueous cleaning is expected to address this issue.

1.14 Successful Closed Loop Installations

Total capital and operating costs for closed loop aqueous cleaning systems can vary greatly depending upon the size and complexity of the systems. It is difficult to

generalize system costs and effectiveness; however, the following case studies and economic data confirm that closed loop systems are economically viable.

Case Study #1

A case study at Superior Plating, Inc. in Minneapolis, MN compared the paybacks for the replacement of a 1,1,2-TCE vapor degreaser with an immersion aqueous cleaning system. The line originally cleaned 15,500 sq.ft. of plated surface per week. Without cleaning solution recovery, the payback for the aqueous cleaning equipment based on operating savings ($13,288/yr) was 1.13 years. When a cleaner recovery system incorporating a ceramic membrane was installed, the operating savings increased to $26,719/yr. The payback period for the total system (immersion tank and recovery system) was only 1.35 years [Karrs and McMonagle, 1993].

Case Study #2

H.C. Stark Inc. (HCST) of Newton, MA is a primary metals company which processes tantalum and niobium from the refining stage to the production of finished parts. HCST used 1,1,1-trichloroethane (TCA) in-house for part vapor degreasing, manual sheet cleaning, and as a full-strength machining coolant. Legislative and employee health considerations prompted HCST to replace TCA with alkaline cleaners and oil-based machining lubricants. By implementing these alternative

technologies, HCST eliminated 40,000 pounds per year of TCA. In addition, the use of ultrafiltration units (spiral wound and hollow fiber) on their cleaning lines has reduced their cleaner purchases from 6,000 pounds per year to 2,000 pounds per year. The payback period for the transition from TCA to the alternative technologies was approximately nine months [TURI Technical Report No.29, 1995].

Case Study #3

The PresMet Corporation of Worcester, MA manufactures a variety of powdered metal parts. Environmental concerns prompted PresMet to implement an aqueous-based cleaning system that eliminated the use of perchloroethylene (perc). Later, PresMet added an ultrafiltration unit for the recovery and recycling of the aqueous cleaner. This cleaner is used primarily in part deburring as a lubricant and rust inhibitor but also removes various contaminants. By implementing aqueous cleaning, PresMet eliminated 24,000 pounds per year of perc. In addition, the use of the ultrafiltration unit has decreased annual cleaner expenditures from $60,000 to $7,500 and the daily volume of deburring effluent discharged to drain from 2,000 gallons to about 75 gallons. The payback on the closed loop system is estimated at two years [TURI Technical Report No.29, 1995].

II. RESEARCH METHODOLOGY

2.1 Introduction

The research objectives of this experimental work were to characterize the composition of various commercially available cleaners and contaminants and to determine which type of filtration system would most effectively remove the contaminants from the cleaning solution after use in various cleaning applications. Based on these two objectives. the overall goal of this research project was evaluate the potential of ultrafiltration to successfully "close the loop" for different aqueous cleaning applications. The methodology proposed to achieve this goal included literature searches and discussions with industry relating to cleaners, contaminants, and filtration units, as well as experimental work at the University of Massachusetts Lowell (UML) and industry sites. The criteria upon which the results were evaluated were oil-surfactant trade-off and membrane fouling rates.

2.2 Cleaner Selection

Determination of the composition of various aqueous cleaners was accomplished by performing literature searches and by discussions with cleaner manufacturers, including Brulin, A.W. Chesterton, W.R. Grace, MacDermid, Oakite, PPG Chemfil, and U.S. Polychemical. An additional source of valuable information was work performed by TURI, in association with the UML Biodegradable Polymer Research Center, on the formulation of an aqueous cleaner that incorporates a biosurfactant. This study examined the exact composition of many commercial aqueous cleaners. Based on this background

information and the final experimental design, a single cleaner from U.S. Polychemical was selected (Polychem A-2000 P) for use in this study.

The majority of cleaners currently available are either fully-emulsifying or oil-rejecting. Fully-emulsifying cleaners form stable oil-in-water emulsions (up to 45-50% oil content in aqueous solution) consisting of oil-swollen micelles uniformly dispersed throughout the cleaner solution. Oil-rejecting cleaners are chemically formulated to emulsify a very low percentage (around 0.5%) of oils. Beyond this "saturation" level, further removal of oil by the cleaner results in the formation of an extremely loose chemical emulsion. When agitation of the cleaner bath is ceased, the oils gradually release from this loose emulsion and form a separate phase [Bernat, 1994]. (Oil-rejecting cleaners have been shown to work poorly in closed loop UF systems, while fully-emulsifying cleaners tend to work quite well [Bernat, 1994].) A-2000 P lies between fully- and oil-rejecting cleaners, and presented an opportunity to evaluate the performance of a new cleaner type. At its suggested use concentration of 5-10% by volume and its suggested temperature range of 130-150°F, this cleaner is theoretically capable of emulsifying all oils in an aqueous bath with oil concentrations up to 5% [Paul, 1996]. Above the 5% emulsification limit, the remaining A-2000 P surfactants (i.e., the surfactants not "tied up" in micelles) will simply serve as wetting agents, which aid in cleaning but leave the remaining oils to exist in a "free" non-emulsified, dispersed state within the aqueous bath. A-2000 P is a non-silicated cleaner which contains nonionic and anionic surfactants. For additional information on A-2000 P, refer to Appendix A.

2.3 Contaminant Selection

Characterization of typical contaminants associated with specific cleaning

applications was achieved through literature searches [McLaughlin, 1995], discussions

with industry (including Citgo Petroleum Inc., Cooks Industrial Lubricants, Park

Chemical Company, and W.A. Wood Company), and by examining the results of industry

polls conducted by the Surface Cleaning Laboratory at TURI. The effects of five

different types of commercially available lubricants on closed loop cleaning system

performance were examined as part of the experimental research for this project. The

five lubricants selected are presented in Table 2. For contaminant compositions refer to

Appendix B.

Table 2. Contaminants Selected for Experimental Study

Product Name	Distributor	Lubricant Classification
Hayes Quench Oil	Park Chemical Company	mineral oil
P Special Lard Oil	W.A. Wood Company	natural oil
Cutting Oil NC 205	Citgo Petroleum Inc.	emulsion
Coolex 40	Cooks Industrial Lubricant	semi-synthetic
Citcool 33	Citgo Petroleum Inc.	synthetic

2.4 Membrane Selection

Background information on membrane filtration units and closed loop aqueous

systems was obtained from direct discussions with equipment manufacturers (U.S. Filter

Corp., Membrex, Inc., Koch Membrane Systems Inc., MSC Liquid Filtration Corp.,

Infinitex Inc, and PROSYS Corp.) and industry reports [LeCarbone, 1993; TURI

Technical Report No.29]. Three types of membranes were selected for evaluation. The

membranes were selected based on pore size and availability. Initially, a spiral-wound polyacrylonitrile (PAN) polymeric membrane module was selected from Membrex with a MWCO of 1,000,000 daltons. (This MWCO corresponds to a pore diameter of 0.1 μm.) The pore size was selected based on conversations with research scientists at Membrex Inc. and with Rob Sheldon, a local Membrex vendor.

After deciding upon the PAN membrane, comparable ceramic and carbon-based membranes were selected (based on availability). A tubular Carbosep® membrane consisting of zirconia oxide ceramic "skin" supported by porous carbon tube was selected from Rhone-Poulenc. This membrane had a pore diameter of 0.14 μm. A tubular carbon fiber-carbon composite (CFCC) membrane was selected from Le Carbone-Lorraine. This membrane had a pore diameter of 0.1 μm.

The Membrex membrane was incorporated into a Membrex ESP-50 unit (on loan from Rob Sheldon), which is capable of processing 50 gpd of oily aqueous cleaning solution. This unit consisted of a 3.5 gpm pump and an MX-1000 high pH PAN membrane. The membrane itself had a surface area of 4,645 cm^2. The unit was modified to incorporate a 0.5 inch inner diameter bleed line. This bleed line, which was throttled with a globe valve, was placed between the pump and the membrane to vary the flow rate through the membrane module. Transmembrane pressure was controlled with a valve located after the module on the retentate line. Figure 5 represents a schematic of the modified ESP-50 unit.
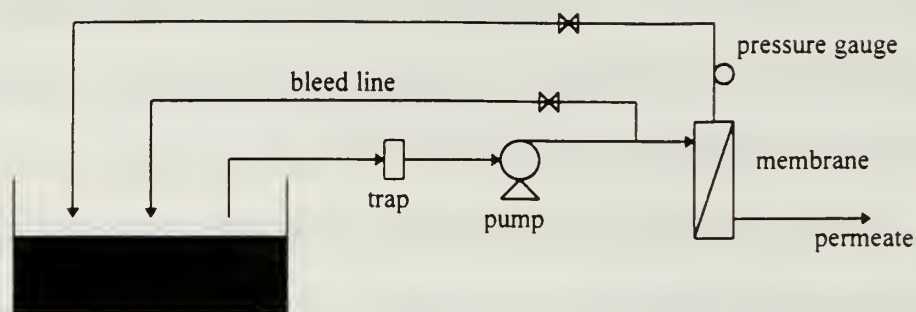
Figure 5. Schematic of Membrex ESP-50 Unit

The Carbosep and CFCC membranes were part of a bench-scale unit located at

PROSYS Corp. The dimensions of the Carbosep membrane was 0.6 cm inner diameter

by 38.1 cm, giving it a surface area of 71.8 cm^2. The dimensions of the CFCC membrane

was 0.6 cm inner diameter by 45.72 cm, giving it a surface area of 86.2 cm^2. The

membranes were used in conjunction with a Cole-Parmer Micropump (model #7144-05).

The pump speed was controlled with a Cole-Parmer Gear Pump Controller (model

#7144-08). In this manner, the system flow rate was varied. Transmembrane pressure

was controlled with a valve located after the membrane module on the retentate line.

Figure 6 represents a schematic of the bench-scale UF system.
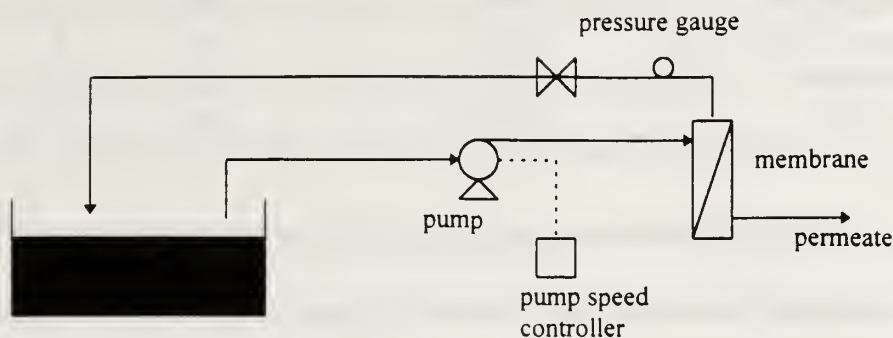
Figure 6. Bench-Scale UF System for Carbosep and CFCC Membranes

2.5 Experimental Methodology

The initial step in the experimental procedure for the evaluation of filtration system performance involved the synthesis of cleaner/contaminant test solutions of known composition, based on cleaner bath compositions typically encountered in industry. The solution compositions by component volumes are listed in Table 3. Cutting Oil NC 205, Coolex 40, and Citcool 33 were received in concentrate form and had to be diluted to a 7% solution by volume in water (16 mL of each contaminant were added to 212 mL of water). The test solutions are 87% water, 10% A-2000 P cleaner, and 3% contaminant or contaminant solution by volume.

Table 3. Test Solution Compositions

Contaminant	Water Volume (mL)	Cleaner Volume (mL)	Contaminant Volume (mL)
Hayes Quench Oil	6612	760	228
P Special Lard Oil	6612	760	228
Cutting Oil NC 205	6824	760	16
Coolex 40	6824	760	16
Citcool 33	6824	760	16

Each test solution was mixed in a 2.5 gallon plastic process tank and heated to its target temperature with a Fisher Scientific Isotemp Immersion Circulator (Model 70). The immersion heater was controlled with an Omega Engineering Inc. Microprocessor Based Controller (Model CN3000). Initially, water fluxes at 130 F and 150 F were determined over a range of flow rates and transmembrane pressures for each of the three membranes. This involved heating tap water to the desired temperature, turning on the feed pump, selecting a feed flow rate through the UF module, and adjusting the valve after the membrane module to vary the transmembrane pressure. Flux readings were taken using a stopwatch and a graduated cylinder. After gathering flux data for water, the test solutions were processed through the three different membranes. Flux data for the solutions were gathered at 140 F over a range of transmembrane pressures at a single feed flow rate. For each of the solutions, a sample of permeate was collected immediately upon system start-up for laboratory analysis. During sampling, the solution temperature was at 140 F and the transmembrane pressure was set at 20 psi. Transmembrane pressures were varied in the same manner as for the tap water runs. After sample collection, flux readings for the solutions were taken using a stopwatch and a graduated cylinder. Note that prior to each run with the five different test solutions, the membranes

were cleaned with a solution of water and A-2000 P, and tap water fluxes were checked. This ensured that each test solution was processed through a "clean" membrane.

After the flux data were gathered, the rate of flux decline over time was recorded for the PAN membrane for the P Special Lard Oil test solution, the Cutting Oil NC 205 test solution, and the Coolex 40 test solution. In this case, the permeate and retentate were both returned to the process tank. Again, the membrane was cleaned prior to processing a new solution. A single flow rate and transmembrane pressure was maintained for the duration of the experimental runs. A relatively low initial flux rate or a rapid decrease in flux rate during test solution processing indicates poor cleaner recyclability for that particular cleaner/contaminant combination. In addition, the rate of flux decline often follows an exponential decline and then levels off to an asymptotic value. Using the following equation [Wankat, 1994]:

$$J_{solv}(t) = (J_{init} - J_{asy})t^m + J_{asy} \qquad (7)$$

(where $J_{solv}(t)$, J_{init}, and J_{asy} are the fluxes at time t, initially, and asymptotically), an empirical constant, m, can be calculated which provides insight into the rate of flux decline for the system for which the flux data were collected. The empirical constant m is negative, and its value corresponds to the rate of flux decline that can be expected for UF membranes. For example, an m = -0.1 corresponds to about a 45% decline in flux in one year, while an m = -0.03 corresponds to about a 16% decline in flux over one year [Wankat, 1994]. In this study, the validity of this equation was tested by calculating

values of m from the test solution rate of flux decline data, and comparing these m values to those presented above.

The samples of permeate gathered during the flux experiments were sent to a laboratory to be analyzed for anionic surfactant concentration and total petroleum hydrocarbon (TPH) concentration. Anionic surfactant concentration was determined by methylene blue active surfactants (MBAS), and TPH concentration was determined by EPA Method 8100. Samples of pure A-2000 P and the five different contaminants were also sent to the laboratory for analysis. The cleaner was analyzed for anionic surfactant concentration, while the contaminants were analyzed for TPH concentration. Note that although the cleaner also contained nonionic surfactants, it was decided that anionic surfactant concentration by itself would still serve as a good indicator of overall surfactant passage through the membranes. By comparing the initial concentrations of surfactants and TPH in the test solutions of known composition with the concentrations in the permeate samples, the oil-surfactant tradeoff was qualitatively evaluated by comparing the amount of surfactant passed through the membrane versus the amount of TPH retained by the membrane. A permeate sample which contained a high surfactant concentration coupled with a low TPH concentration signified good cleaner recyclability for that particular cleaner/contaminant combination.

III. EXPERIMENTAL RESULTS & DISCUSSION

The following tables and figures present the experimental data collected for this study. Note that the test solutions have abbreviated names in Tables 12 through 18 and Table 20. The test solution contaminants and corresponding names are listed in Table 4.

Table 4. Test Solution Contaminants and Corresponding Names

Contaminant	Solution Name
Hayes Quench Oil	HQO
P Special Lard Oil	PSL
Cutting Oil NC 205	CONC
Coolex 40	COOL
Citcool 33	CIT
Tap Water and A-2000 P Only	2000P

The data in Tables 5 through 10, 12 through 15, 17, and 18 have been graphically represented in Figures 7 through 20. Note that the legend in Figures 7 through 9 and 13 through 15 contains the notation "high", "int.", and "low". These notations refer to the high, intermediate, and low feed flow rates into the membrane modules which were used during the flux data experiments. These flow rates are listed with the data tables from which the graphs were generated.

3.1 Tap Water Fluxes

Tables 5 through 10 contain the data for tap water fluxes through the three different membranes at different temperatures. Figures 7, 8, and 9 illustrate the effect of increasing transmembrane pressure and temperature on flux for tap water. For all three

membranes, the curves are approximately linear, which is to be expected. As shown in Equation (4):

$$v = Q_m(\Delta p - \Delta \pi)\mu_{H2O}/\mu \qquad (4)$$

the volumetric flux v is proportional to the difference between the transmembrane pressure drop Δp and the net osmotic pressure $\Delta \pi$ across the UF membrane. In the case of tap water, $\Delta \pi$ approaches zero and Equation (4) can be reduced to $v = Q_m(\Delta p)\mu_{H2O}/\mu$. The viscosity correction factor is necessary because the viscosity of water varies with temperature. It follows that at a given temperature μ_{H2O}/μ will be constant, and the flux should vary linearly with transmembrane pressure drop. Therefore a permeability (Q_m) can be calculated for each membrane (see Table 11) based on experimental flux values.

The tap water fluxes demonstrate that each membrane has its own characteristic flux curve. The differences in the curves can be attributed to the fact that each membrane has its own distinct values of D (average pore size), ε (membrane void fraction), L (nominal thickness of the active layer of the membrane), and τ (membrane tortuosity factor). As stated, the result of these intrinsic differences is that each membrane will have its own characteristic permeability, and thus its own characteristic flux curve.

Overall, the PAN membrane had the lowest flux rates, even though it appeared to have a greater permeability than the Carbosep membrane. However, the permeability of the Carbosep membrane calculated from the experimental data may be low. The Carbosep membrane had been previously used for bench-testing at PROSYS Corporation, and may have been partially fouled. If the membrane was not thoroughly cleaned prior to experimentation, the material which fouled the Carbosep membrane may have reformed a

gel layer when exposed to water. The gel layer would create a resistance to filtration and could cause the Carbosep membrane to begin approaching its limiting flux value at transmembrane pressure drops as low as 5 to 10 psi. The permeability calculated for the Carbosep membrane was based on flux data taken over transmembrane pressure drops of 5 to 25 psi. At these pressures, the fluxes may have almost reached the limiting flux value (refer to Section 1.8). Accordingly, the slopes of these flux curves would have smaller values than the slopes of the flux curves for a clean Carbosep membrane. It follows that the permeability calculated from the slopes of the experimental flux curves would be lower than the permeability of a clean Carbosep membrane.

The flux rates for the Carbosep and CFCC membranes were comparable at intermediate transmembrane pressures (i.e., 15 psi) at 130F, but the slope of the flux curve for the CFCC membrane was much greater (indicating a greater permeability for the CFCC membrane). At 150F, the same trend was observed, but the transmembrane pressure at which the fluxes were comparable dropped to 10 psi. However, it must again be noted that the permeability calculated for the Carbosep membrane from the experimental data may be lower than its actual permeability. It is interesting to note that the PAN membrane shows a slight decrease in the expected flux at higher transmembrane pressure drops. This may be due to the fact that the membrane is polymeric. At higher transmembrane pressure drops, the PAN membrane may possibly be compressed, resulting in a decrease in effective pore size. Such a decrease in pore size would decrease the membrane permeability (as noted in Section 1.8), thus decreasing the flux through the membrane.

The effect of varying feed flow rates into the membrane modules is clearly indicated in Figures 7, 8, and 9. As stated in Section 1.8, the limiting flux value can be increased by increasing the tangential feed flow velocity in the crossflow system.   For each membrane, an increase in feed flow rate produced an increase in flux at a given transmembrane pressure drop.

Table 5. Tap Water Fluxes for PAN Membrane at 130 F in mL/cm^2*hr at Different Feed Flow Rates

Transmembrane Pressure	@ 10350 mL/min	@ 6400 mL/min	@ 2440 mL/min
10 psi	11.0	10.9	10.3
15 psi	19.0	18.9	18.1
20 psi	26.1	25.8	25.4
25 psi	30.2	30.0	29.5

Table 6. Tap Water Fluxes for PAN Membrane at 150 F in mL/cm^2*hr at Different Feed Flow Rates

Transmembrane Pressure	@ 10350 mL/min	@ 6400 mL/min	@ 2440 mL/min
10 psi	12.4	12.3	11.9
15 psi	20.9	20.7	20.3
20 psi	27.1	26.9	26.6
25 psi	32.6	32.3	31.8

Table 7. Tap Water Fluxes for Carbosep Membrane at 130 F in mL/cm^2*hr at Different Feed Flow Rates

Transmembrane Pressure	@ 1680 mL/min	@ 1380 mL/min	@ 990 mL/min
5 psi	20.1	15.0	11.7
10 psi	25.1	21.7	16.7
15 psi	30.1	26.7	21.7
20 psi	35.9	31.8	28.4
25 psi	40.1	36.8	34.3

Table 8. Tap Water Fluxes for Carbosep Membrane at 150 F in mL/cm^2*hr at Different Feed Flow Rates

Transmembrane Pressure	@ 1680 mL/min	@ 1380 mL/min	@ 990 mL/min
5 psi	25.1	23.4	13.4
10 psi	28.4	25.1	20.1
15 psi	31.6	28.4	23.4
20 psi	35.9	32.6	29.2
25 psi	40.1	37.6	35.1

Table 9. Tap Water Fluxes for CFCC Membrane at 130 F in mL/cm^2*hr at Different Feed Flow Rates

Transmembrane Pressure	@ 1740 mL/min	@ 1380 mL/min	@ 960 mL/min
5 psi	8.4	8.4	7.0
10 psi	18.8	18.8	14.6
15 psi	30.6	29.2	23.0
20 psi	42.5	41.1	32.0
25 psi	54.3	52.2	39.7

Table 10. Tap Water Fluxes for CFCC Membrane at 150 F in mL/cm^2*hr at Different Feed Flow Rates

Transmembrane Pressure	@ 1740 mL/min	@ 1380 mL/min	@ 960 mL/min
5 psi	13.2	8.4	7.7
10 psi	28.5	21.6	16.0
15 psi	43.2	36.2	26.5
20 psi	59.2	54.3	34.1
25 psi	73.1	65.4	44.5

Table 11. Membrane Permeabilities

Membrane Type	Average Permeability (mL/cm^2*hr)*psi^{-1}
PAN	0.83
Carbosep	0.55
CFCC	1.30

Figure 7. Tap Water Fluxes for PAN Membrane

Figure 8. Tap Water Fluxes for Carbosep Membrane

130F-high
130F-int
130F-low
150F-high
150F-int
150F-low

Transmembrane Pressure (psi)

Flux (mL/cm2·hr)
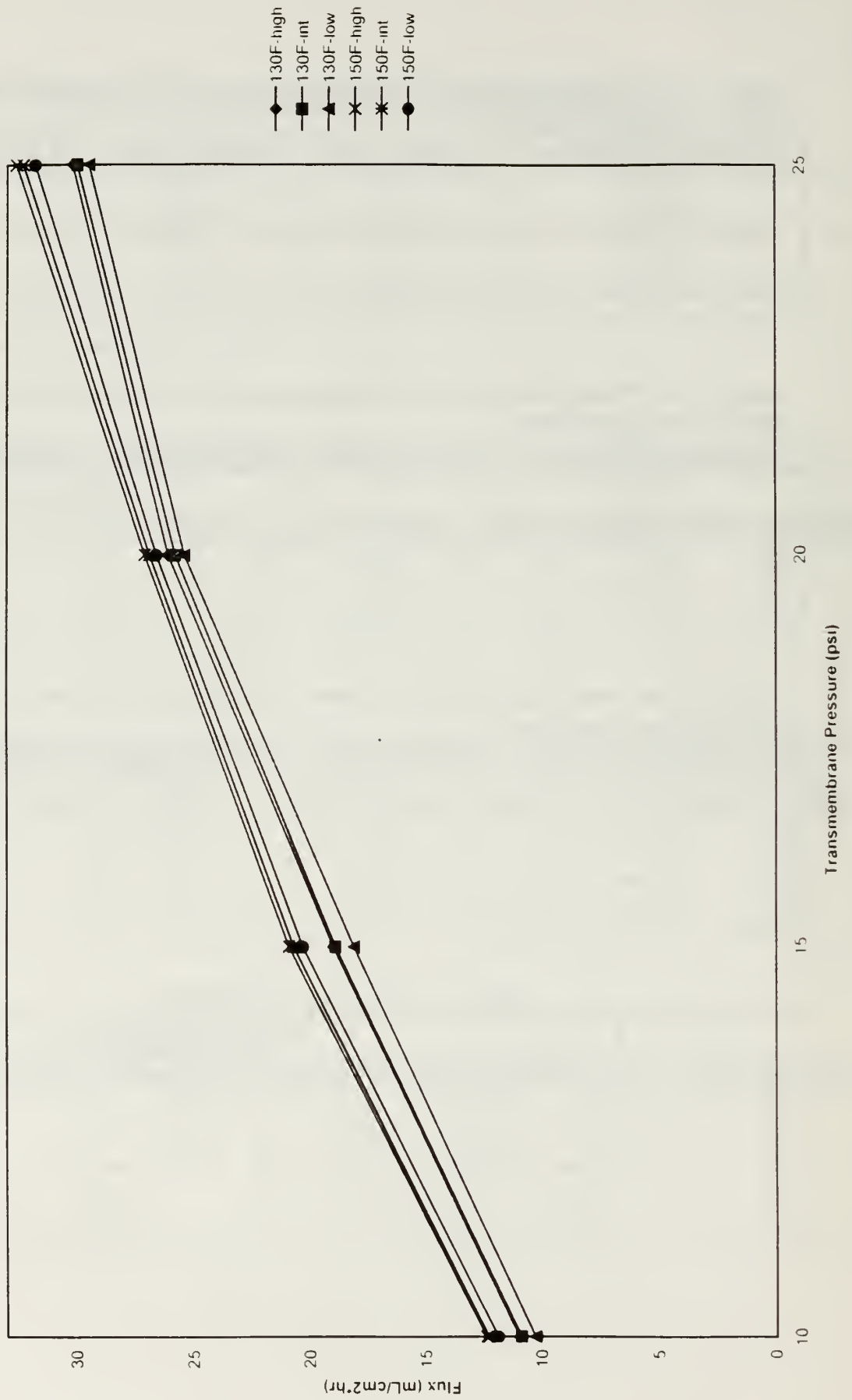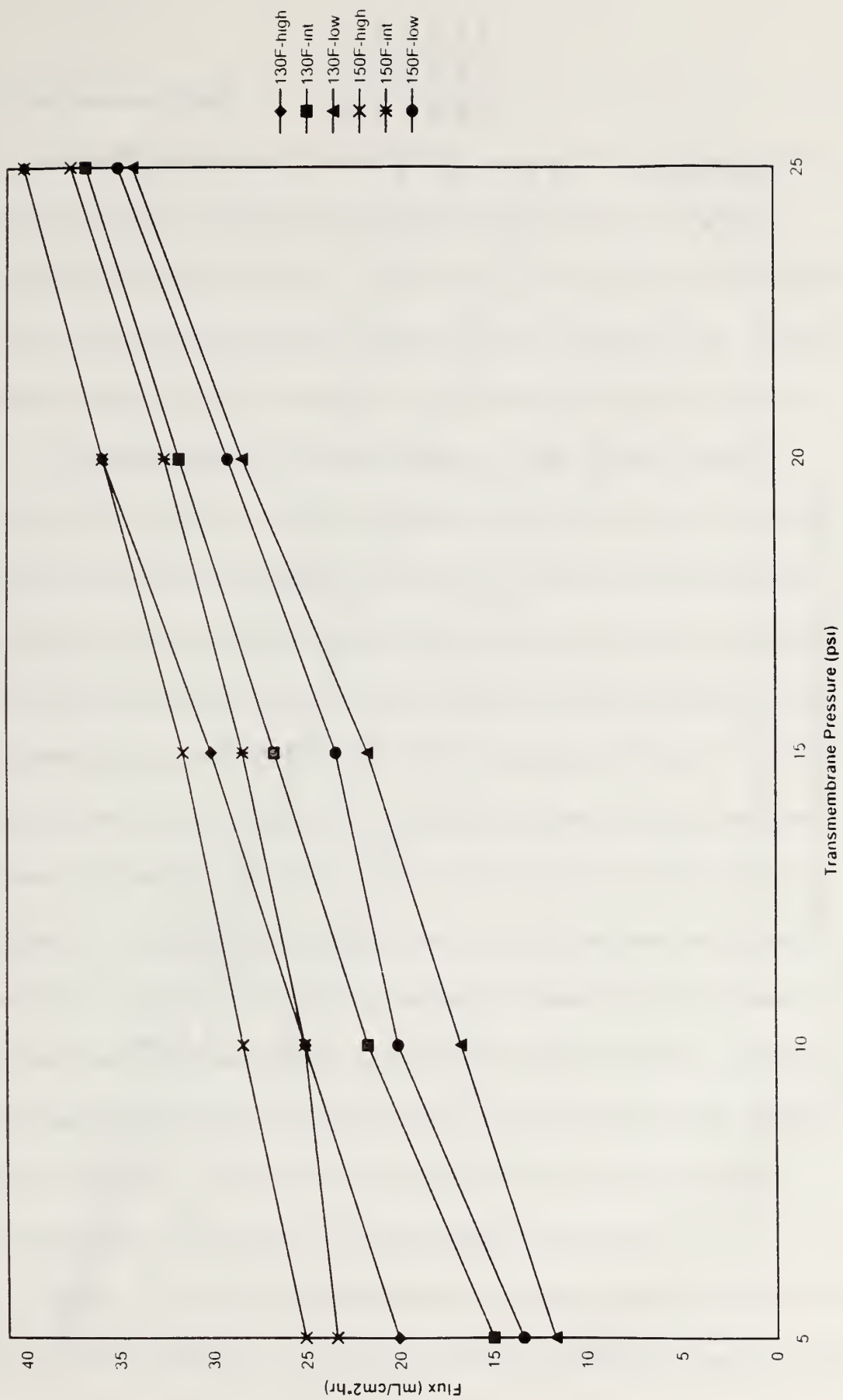
Figure 9. Tap Water Fluxes for CFCC Membrane
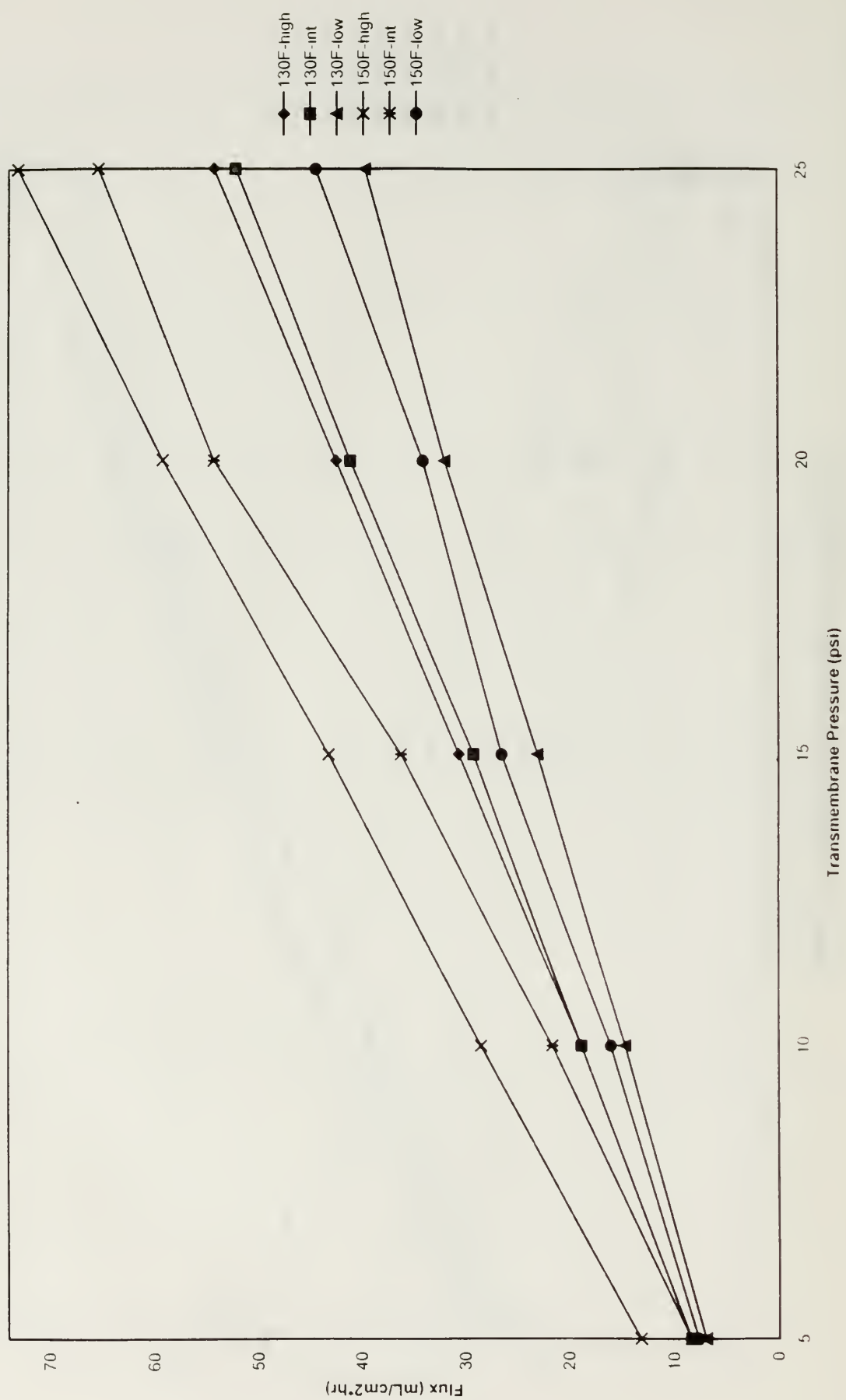
3.2 Test Solution Fluxes

Tables 12 through 14 provide the data for test solution fluxes through the three

different membranes. Figures 10 through 17 illustrate the effect of increasing

transmembrane pressure on flux for the test solutions. In the case of the PAN membrane,

the flux was determined over a range of membrane module feed flow rates. The fluxes

for the Carbosep and CFCC membranes were determined at a single feed flow rate.

The majority of the flux curves exhibit the curvature expected at higher

transmembrane pressures. As the transmembrane pressure increases and more water-

cleaner solution is forced through the membrane, the concentration of the rejected

contaminants increases at the surface of the membrane (i.e., concentration polarization).

The increase in contaminant concentration at the membrane may eventually result in

membrane fouling or the formation of a gel layer as described in Section 1.7. As this gel

layer forms and increases in thickness, the hydraulic resistance across the membrane

increases [McCabe et al, 1993]. Eventually, a steady-state flux is achieved, which is

independent of increasing transmembrane pressure. (As Δp increases, so does the

thickness of the gel layer, which in turn continues to increase hydraulic resistance across

the membrane.) This phenomena can easily be seen in Figure 16 for the test solutions

containing Hayes Quench Oil, P Special Lard Oil, and Cutting Oil NC 205. However, the

majority of the flux curves did not reach steady-state values, most likely because

transmembrane pressures were not increased to high enough levels.

Figures 13, 14, and 15 illustrate the effect of varying membrane feed flow rates on

flux for the PAN membrane. For a given test solution, the overall flux increased as the

feed flow rate was increased. This is to be expected since this increased flow rate through

the membrane module serves to strip away any retained emulsified oils from the

membrane surface which could result in fouling and/or gel layer formation [McCabe et al,

1993].

The flux decline curves in Figure 18 illustrate a rapid decrease in flux for the PAN

membrane for the P Special Lard Oil, Cutting Oil NC 205, and Coolex 40 test solutions.

These curves were generated from data listed in Table 15. As stated earlier, the data

listed in Table 15 can be fit to Equation 7 from Section 2.5. After the data were fit, the

resulting values for m were listed in Table 16. As the values of m suggest, and as the data

supports, the test solutions exhibited a very rapid decline in flux to an asymptotic value.

The m values calculated from this data verify the validity of Equation 7. The Coolex 40

solution flux declined the most slowly and maintained the highest asymptotic flux value,

followed by the P Special Lard Oil and Cutting Oil NC 205 solutions. These curves agree

with the flux data gathered while varying transmembrane pressure (i.e., the Coolex 40

solution had the highest overall flux, followed by the P Special Lard Oil and Cutting Oil

NC 205 solutions). The Coolex 40 solution contained the lowest concentration of

petroleum oils, and therefore should exhibit the slowest fouling/gel layer formation rates

(and thus slower flux decline) and the highest asymptotic flux (due to a lesser extent of

overall fouling/gel layer thickness). The Cutting Oil NC 205 solution exhibited the most

rapid flux decline and the lowest asymptotic flux value. Although Cutting Oil NC 205

contains a lower concentration of petroleum oils than P Special Lard Oil, it is possible

that the Cutting Oil NC 205 may have contained non-oil additives which may have fouled

the membrane or caused the PAN membrane to swell, thus causing the pore diameters to decrease. (As stated in Section 1.6, certain chemical compounds are incompatible with polymeric membranes). Although these curves indicate a rapid decline in flux over a short period of time for the three test solutions, the percentage of flux lost (17.7% for the Coolex 40 solution, 11.6% for the P Special Lard Oil solution, and 8.0% for the Cutting Oil NC 205 solution) is not so great as to preclude the possibility of using a closed loop UF system to recycle the cleaner for each of the three test solutions.

Overall, the fluxes for the test solutions containing contaminants with high concentrations of petroleum oils (i.e., Hayes Quench Oil, P Special Lard Oil, and Cutting Oil NC 205) were much lower than those for tap water. This is to be expected since the retained emulsified oils would contribute to membrane fouling and/or gel layer formation. It is interesting to note that the test solutions containing Coolex 40, Citcool 33, and cleaner only exhibited flux curves similar to those for tap water, although the fluxes were still overall somewhat lower for these test solutions, as is expected since some contaminants would be present in the retentate (and thus contribute to membrane fouling and/or gel layer formation). Coolex 40 is semi-synthetic and contains only a small percentage of petroleum oil-based fluids, while Citcool 33 contains only synthetic fluids. These contaminants contain a majority of components which are small enough to pass through the membrane pores (refer to Appendix B). As for the cleaner only test solution, these high fluxes suggest that very little of the cleaner components is being retained. This implies that the recyclability of the aqueous cleaner itself is good.

In comparing the fluxes for the different membranes, the CFCC membrane has significantly higher fluxes for the Coolex 40, Citcool 33, and cleaner only test solutions than the PAN and Carbosep membranes; further, the Carbosep membrane produced slightly higher fluxes than the PAN membrane. This membrane performance is similar to that for tap water (the reason for this was described earlier in this section). As for the fluxes for the Hayes Quench Oil, P Special Lard Oil, and Cutting Oil NC 205 test solutions, the performance of the PAN and CFCC membranes were comparable, while the Carbosep fluxes were much lower. The higher fluxes with the PAN membrane for these test solutions can be attributed to the hydrophilicity of the membrane, which assisted it in resisting the fouling and/or gel layer formation which occurred in the case of the other two membranes. This hydrophilicity causes oily contaminants to be repelled from the membrane surface.

Table 12. Test Solution Fluxes for PAN Membrane at 140 F in mL/cm²*hr

Feed Flow Rate: 10350 mL/min.

Transmembrane Pressure (psi)	HQO	PSL	CONC	COOL	CIT	2000P
10	6.6	8.5	5.8	11.2	10.5	9.3
15	12.8	14.3	11.2	18.6	18.6	17.8
20	15.9	19.4	15.9	24.4	24.8	24.6
25	19.4	21.7	20.2	29.5	29.8	30.2

Feed Flow Rate: 6400 mL/min

Transmembrane Pressure (psi)	HQO	PSL	CONC	COOL	CIT	2000P
10	4.8	7.3	4.7	9.6	9.5	9.1
15	11.1	12.1	10.6	16.3	16.4	16.6
20	14.6	15.4	12.7	23.1	22.3	23.0
25	18.7	18.6	16.7	26.3	25.6	29.5

Feed Flow Rate: 2440 mL/min

Transmembrane Pressure (psi)	HQO	PSL	CONC	COOL	CIT	2000P
10	5.8	7.1	3.8	8.6	8.7	8.2
15	9.1	11.1	8.6	14.7	14.9	13.9
20	13.1	13.8	11.6	19.2	19.7	20.3
25	15.4	17.4	14.1	23.6	24.7	25.5

Table 13. Test Solution Fluxes for Carbosep Membrane at 140 F in mL/cm²*hr

Feed Flow Rate: 1680 mL/min

Transmembrane Pressure (psi)	HQO	PSL	CONC	COOL	CIT	2000P
5	2.5	0.8	1.7	10.0	10.9	11.7
10	4.2	2.5	3.3	11.7	13.4	13.4
15	5.8	4.2	4.2	12.5	15.9	15.9
20	6.7	5.0	5.8	15.0	18.4	19.2
25	6.7	5.8	6.7	17.5	21.7	22.6
30	6.7	5.8	6.7	20.9	25.1	25.9

Table 14. Test Solution Fluxes for CFCC Membrane at 140 F in mL/cm^2*hr

Feed Flow Rate: 1740 mL/min

Transmembrane Pressure (psi)	HQO	PSL	CONC	COOL	CIT	2000P
5	2.1	1.4	3.5	7.7	7.7	16.7
10	4.2	3.5	7.0	20.9	19.5	36.2
15	6.3	4.9	8.4	33.4	30.0	58.5
20	9.7	7.0	10.4	43.2	41.1	79.4
25	13.9	8.4	11.8	57.8	52.2	91.9
30	16.7	8.4	17.4	69.6	62.6	100.2

Table 15. Flux Decline Data for PAN Membrane at 140 F in mL/cm^2*hr (ΔP=20 psi)

Time (days)	PSL	CONC	COOL
0	19.8	18.7	22.0
1	18.9	17.4	20.8
2	18.2	17.4	20.0
3	17.7	17.3	19.4
4	17.6	17.3	18.3
5	17.6	17.3	18.1
6	17.5	17.2	18.1

Table 16. Flux Decline Data m Values

Test Solution	m Value
PSL	-1.083
CONC	-1.834
COOL	-0.655

Figure 10. Test Solution Fluxes for PAN Membrane at High Feed Flow Rate and 140F
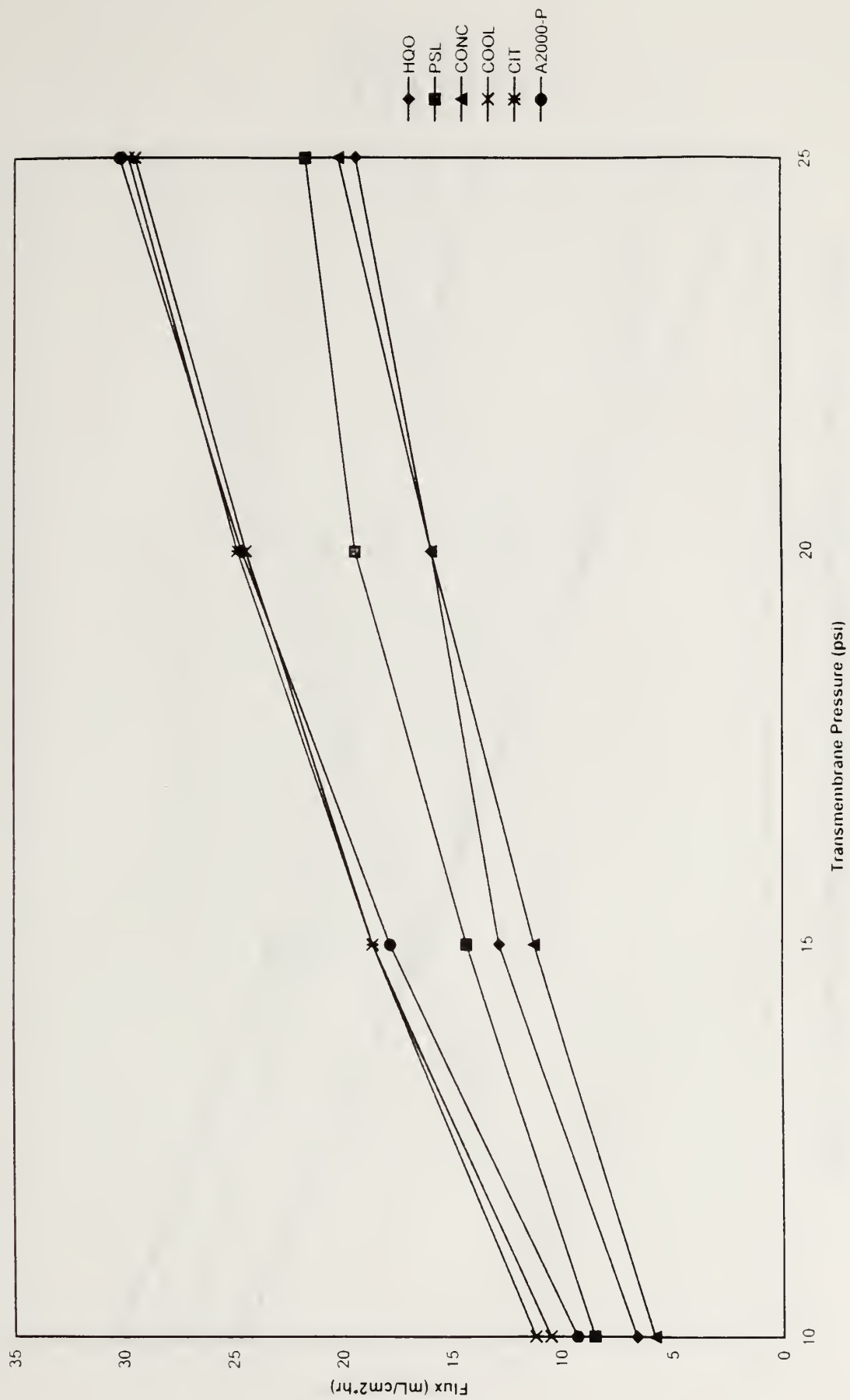
Figure 11. Test Solution Fluxes for PAN Membrane at Intermediate Feed Flow Rate and 140F

47
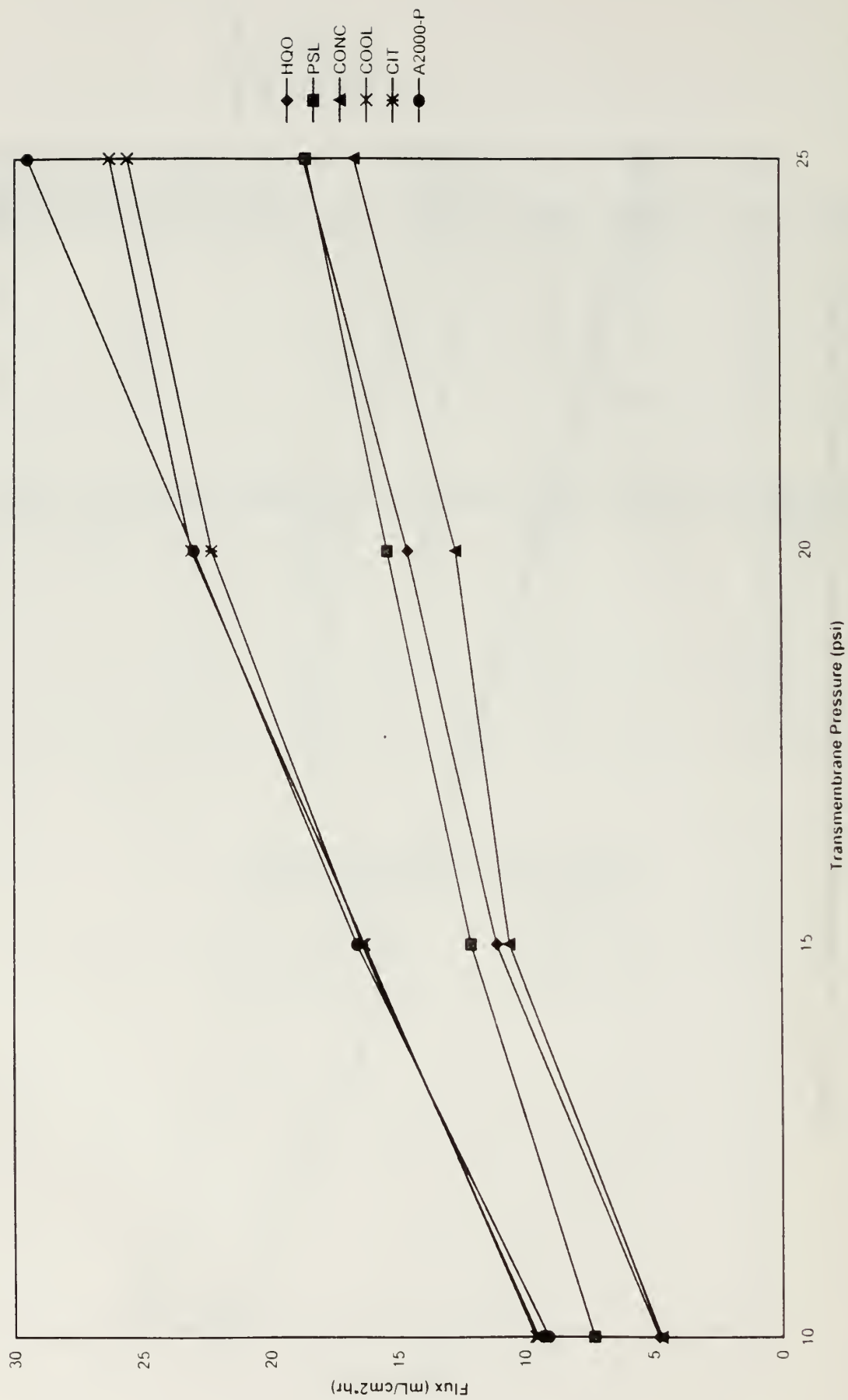
Figure 12. Test Solution Fluxes for PAN Membrane at Low Feed Flow Rate and 140F

48
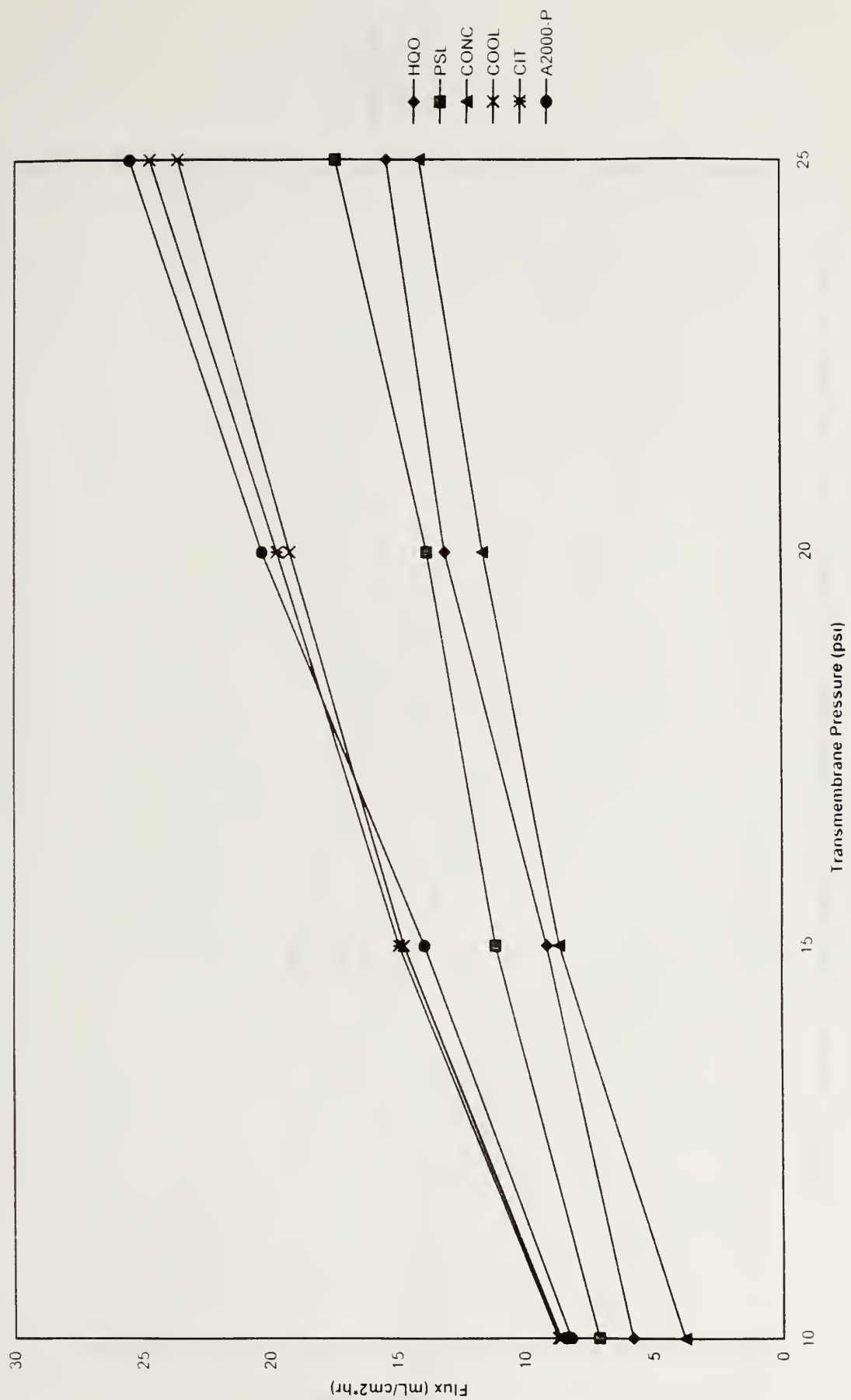
Figure 13. Citcool 33 Flux Rates for PAN Membrane Over a Range of Feed Flow Rates and 140F

Figure 14. P-Special Lard Oil Flux Rates for PAN Membrane Over a Range of Feed Flow Rates and 140F
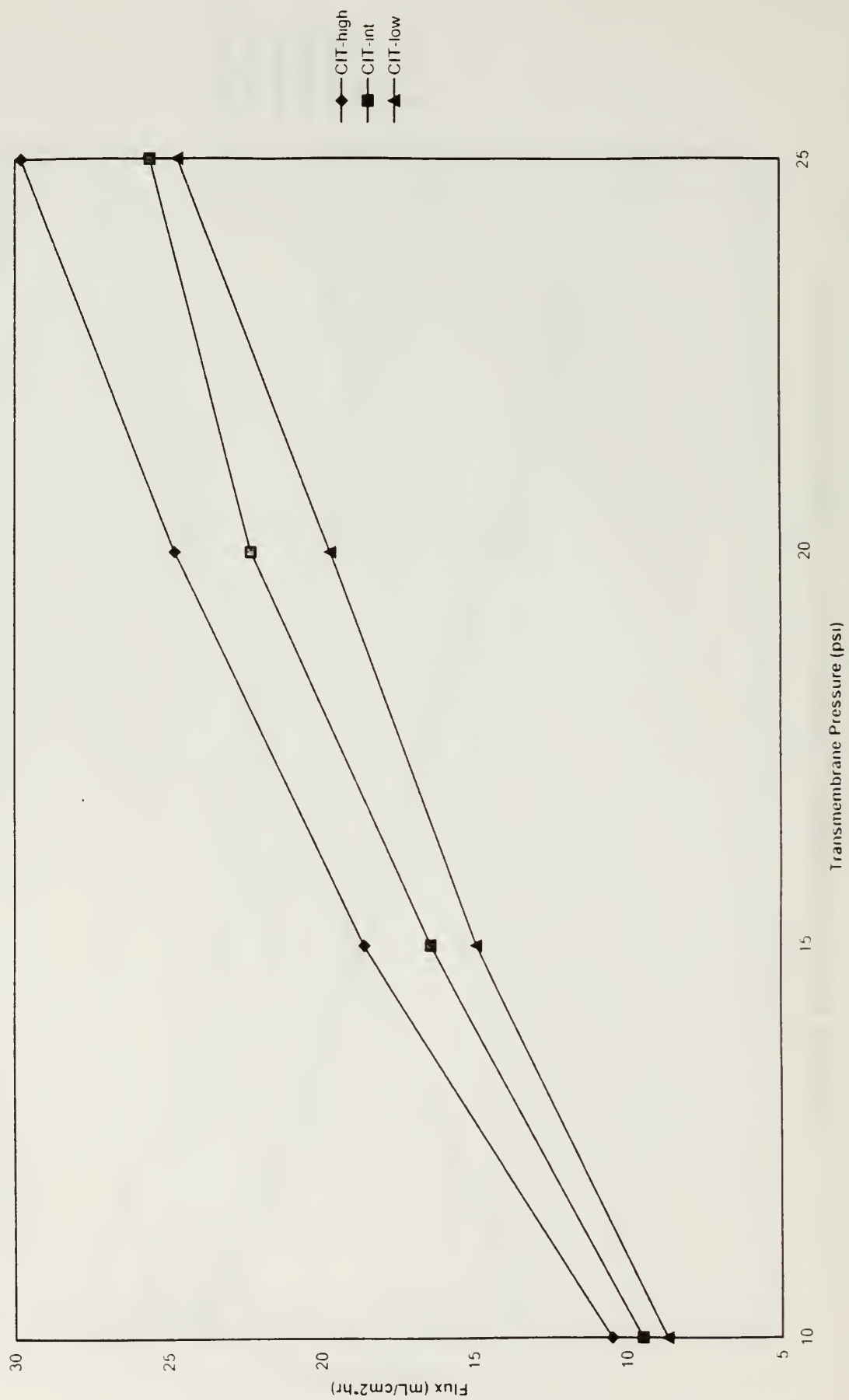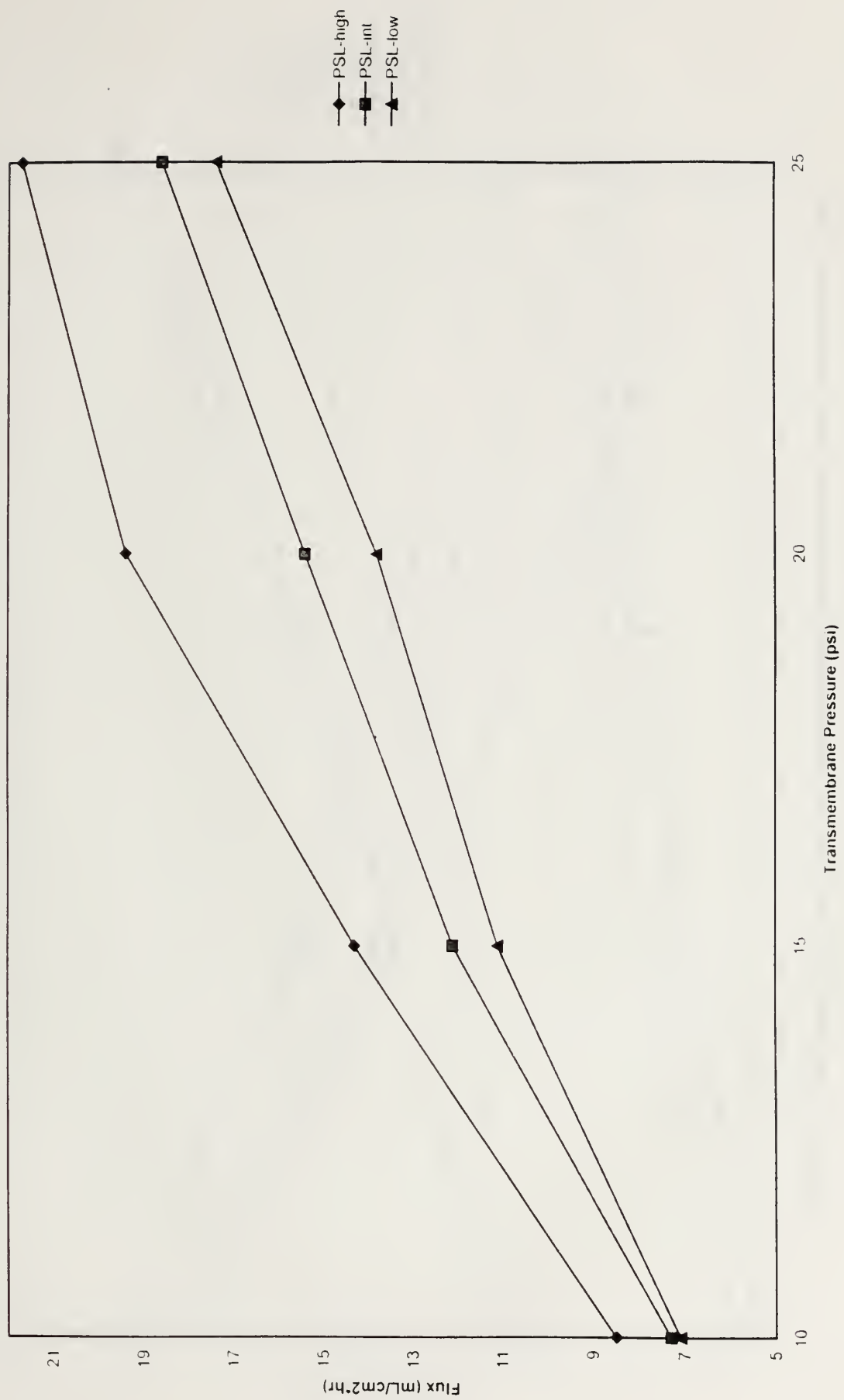
50

Figure 15. Cutting Oil NC 205 Flux Rates for PAN Membrane Over a Range of Feed Flow Rates and 140F
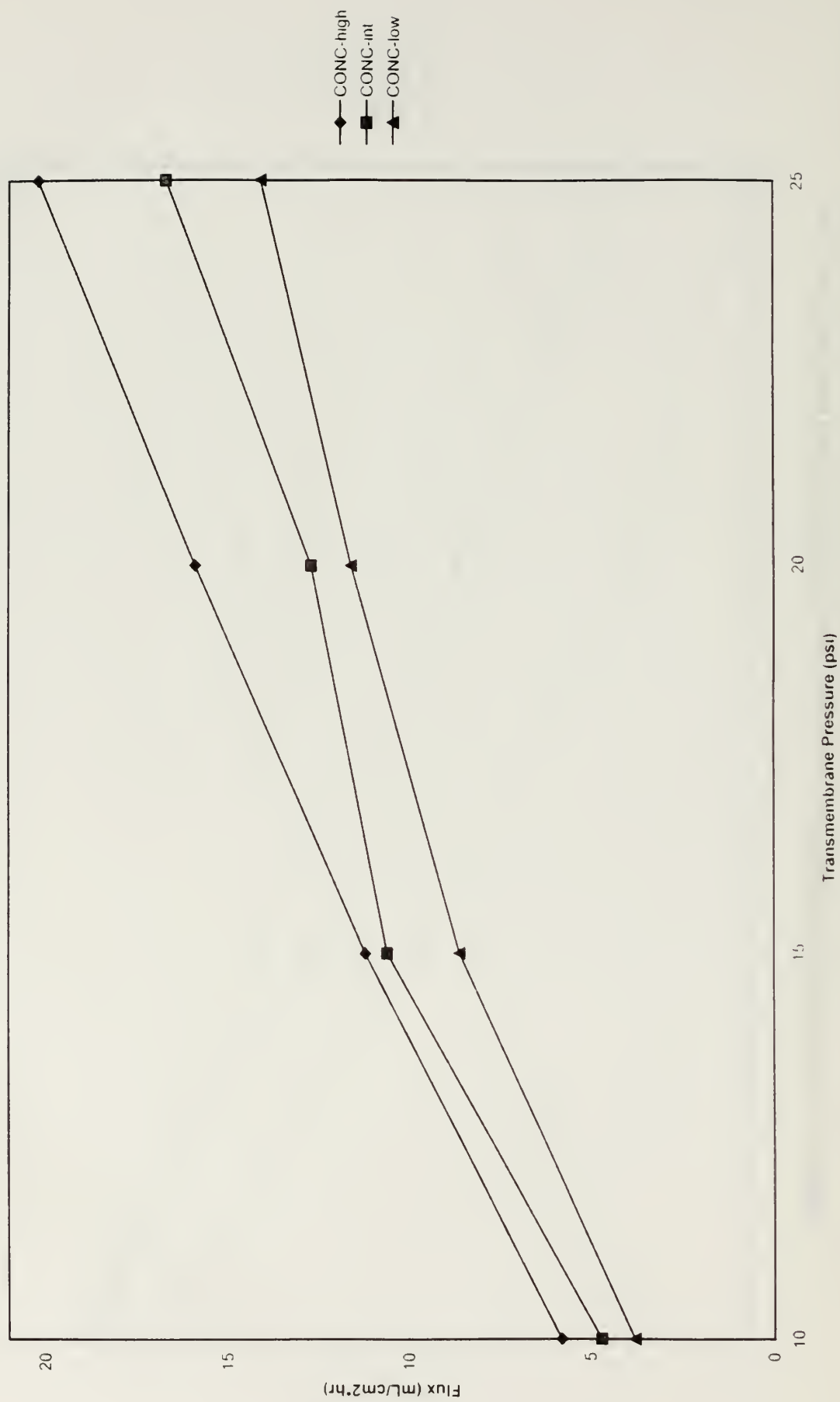
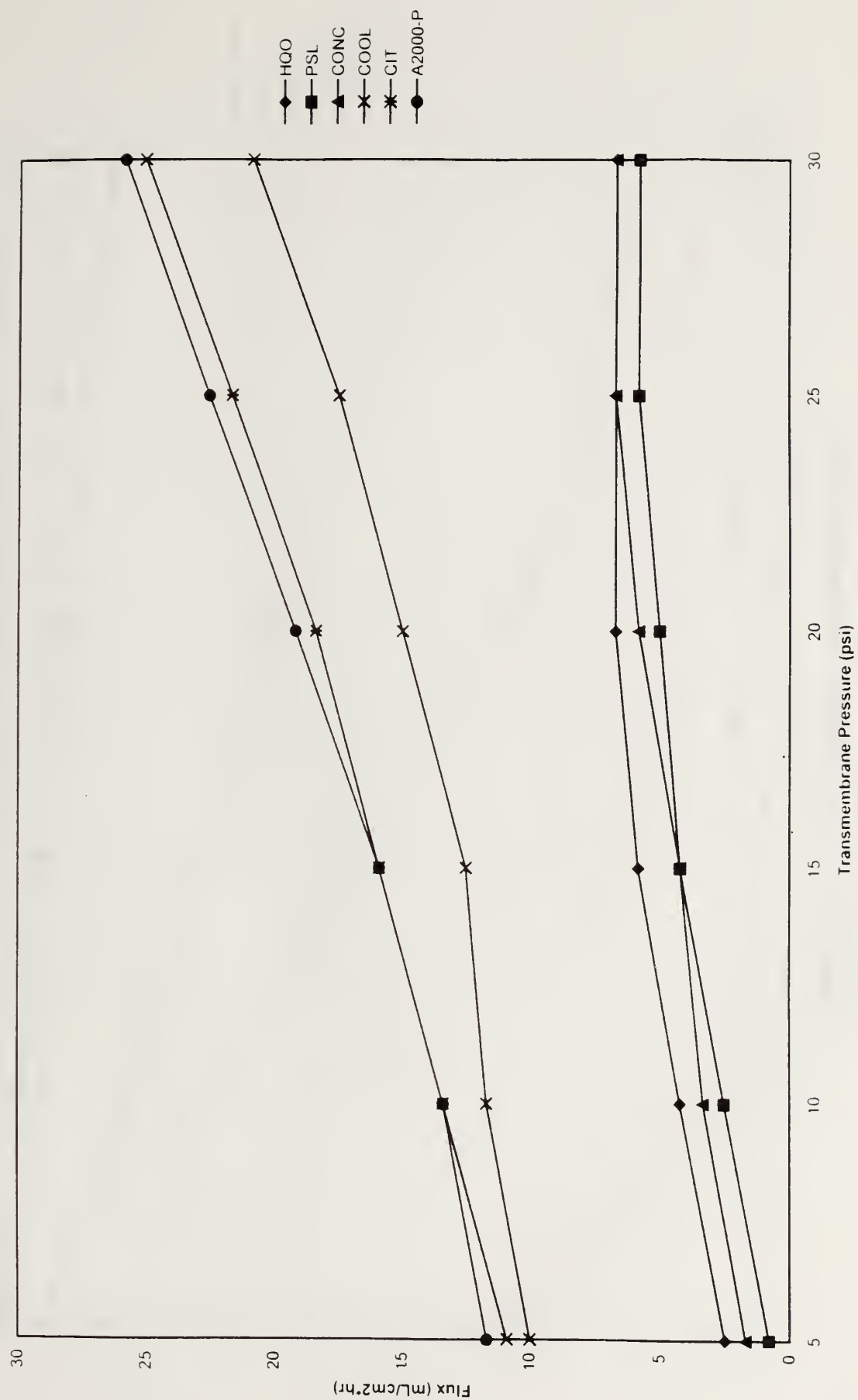Figure 16. Test Solution Fluxes for Carbosep Membrane at 140F

Figure 17. Test Solution Fluxes for CFCC Membrane at 140F

53
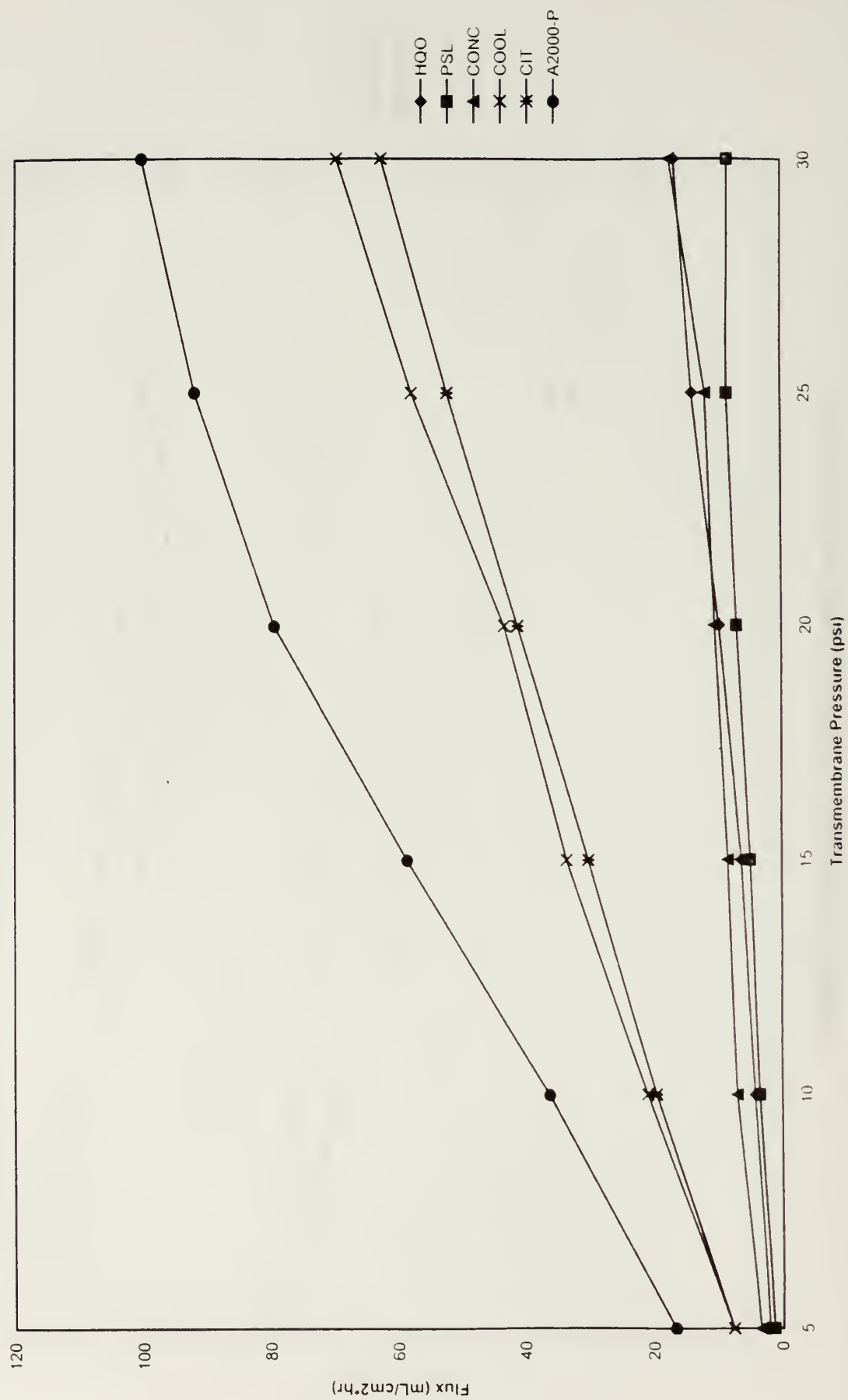
Figure 18. Rate of Flux Decline for Test Solutions with PAN Membrane

54
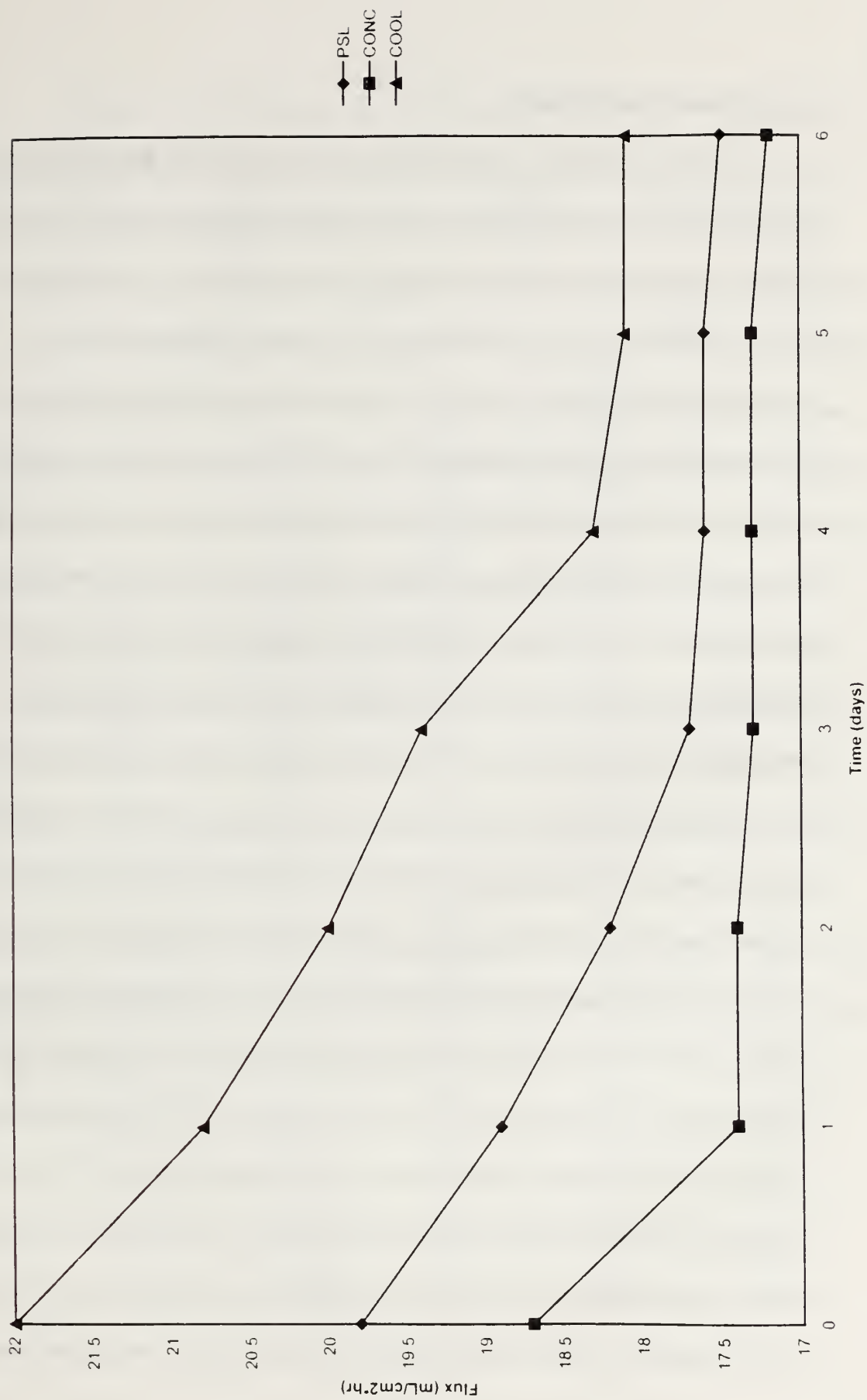
3.3 Oil-Surfactant Tradeoff

Table 17 contains the anionic surfactant concentrations of the permeate samples, while Table 18 contains the TPH concentrations for the permeate samples. The permeate samples were taken during the test solution flux data experiments. For comparison, a 10% by volume solution of A-2000 P and tap water had an anionic surfactant concentration of 1,110 mg/L. The TPH concentrations for the pure contaminants and for the contaminant test solutions are listed in Table 19. (For test solution compositions refer to Section 2.5.) Figures 19 and 20 graphically represent the anionic surfactant and total petroleum hydrocarbon (TPH) concentrations, respectively, in the permeate samples taken for each of the three membranes. The laboratory analysis of the permeate samples revealed that, for Hayes Quench Oil and P Special Lard Oil, the retention of the petroleum-based portion of the contaminants by all three of the membranes is greater than 99%. In the case of Coolex 40 and Citcool 33, the permeate analysis indicates that more petroleum-based contaminants were present in the permeate samples than in the actual Coolex 40 and Citcool 33 test solutions. This is most likely the result of the membranes not being totally cleaned between experimental runs (i.e., the membranes, and thus the permeate samples, were contaminated with small amounts of Hayes Quench Oil, P Special Lard Oil, or Cutting Oil NC 205). For Cutting Oil NC 205, the percentage retention of petroleum-based contaminants varies from approximately 70% to 90%. Again there is the issue that the membranes may not have been adequately cleaned between runs. In addition, for Cutting Oil NC 205, Coolex 40, and Citcool 33, a portion of the components in the contaminants are small enough to pass through the membranes.

Based on the test solution anionic surfactant concentration of 1,110 mg/L, the percentage passage of anionic surfactant for all the samples is listed in Table 20. As indicated in Table 20, the passage of anionic surfactant through the three different membranes varied. The surfactant passage for the PAN membrane ranged from 67 % to 88%; for the Carbosep membrane, passage ranged from 53% to 66%; and for the CFCC membrane, passage ranged from 87% to 95%. Note that the relatively low surfactant passage for the Carbosep membrane is most likely the result of the fact that the permeate samples drawn from the Carbosep and CFCC membranes were taken from the same test solution (i.e., a single 7,600 mL test solution was first processed through the CFCC membrane to obtain a permeate sample, with the remaining test solution then being processed through the Carbosep membrane). Note that the permeate samples for the Carbosep membrane were taken *after* the CFCC membrane permeate samples. (The majority of free surfactants were most likely removed from the test solutions in the CFCC membrane permeate samples.) If new test solutions had been used for the Carbosep permeate samples, comparable surfactant passages would likely be seen. At such levels of surfactant passages and oil rejections, it appears that for these test solutions, a closed loop UF system could be economically justifiable.

Table 17. Test Solution Permeate Samples Surfactant Concentrations (mg/L)

Membrane Type	HQO	PSL	CONC	COOL	CIT
PAN	925	975	938	908	743
Carbosep	735	705	712	592	607
CFCC	1023	990	1050	1005	967

Table 18. Test Solution Permeate Samples TPH Concentrations (mg/L)

Membrane Type	HQO	PSL	CONC	COOL	CIT
PAN	174	122	112	12.6	83.7
Carbosep	36.8	130	36.8	20.2	19.9
CFCC	14.7	20.8	68.3	6.3	16.8

Table 19. TPH Concentrations for Contaminants and Test Solutions

Contaminant	TPH Conc. of Pure Contaminant (mg/L)	TPH Conc. of Test Solution (mg/L)
Hayes Quench Oil	833,000	24,990
P Special Lard Oil	591,000	17,730
Cutting Oil NC 205	175,000	368
Coolex 40	3,900	8.2
Citcool 33	0	0

Table 20. Percentage of Anionic Surfactant Passage for Permeate Samples

Membrane Type	HQO	PSL	CONC	COOL	CIT
PAN	83	88	85	82	67
Carbosep	66	64	64	53	55
CFCC	92	89	95	91	87

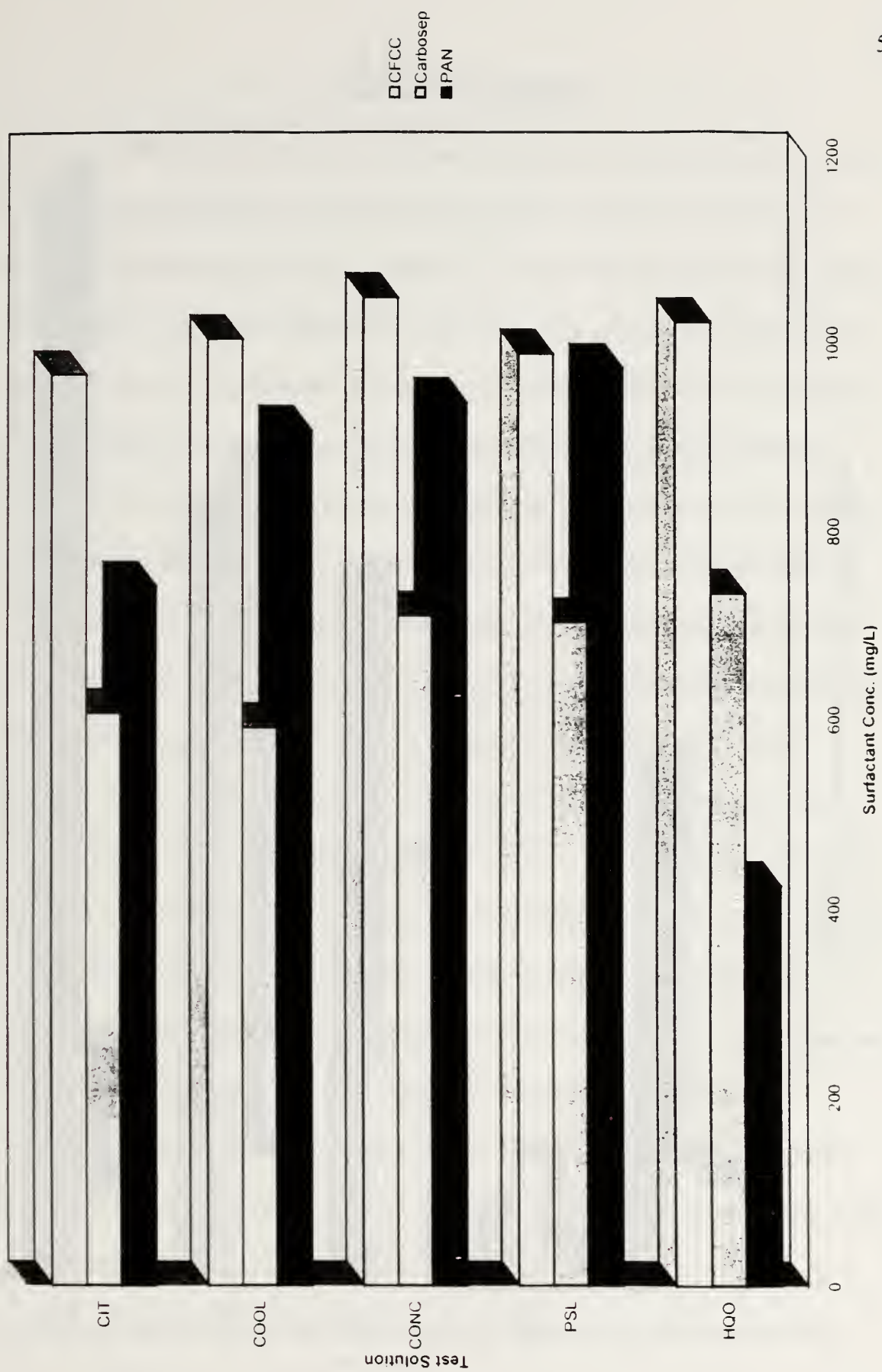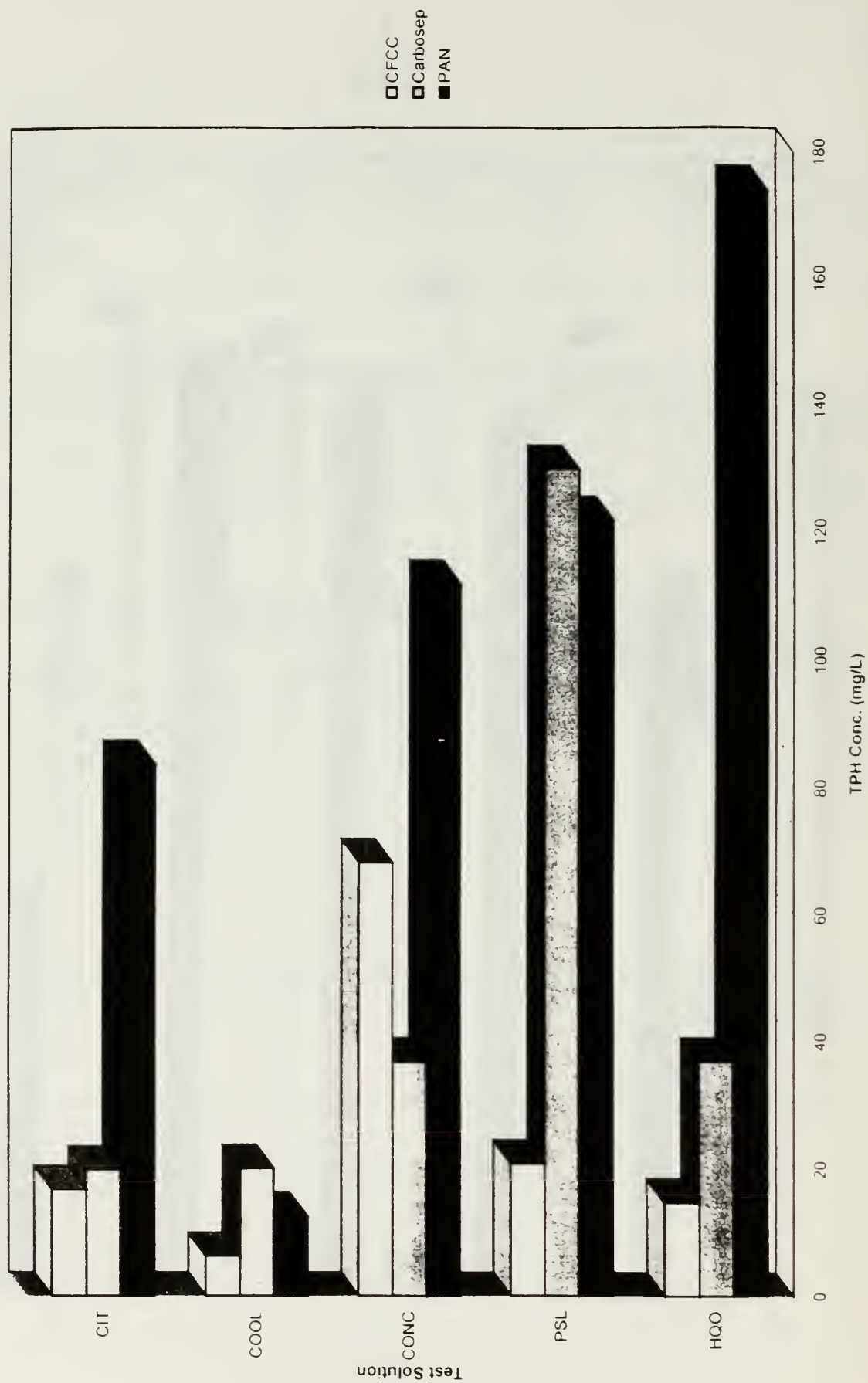Figure 19. Anionic Surfactant Concentrations in Permeate Samples

Figure 20. TPH Concentrations in Permeate Samples

59

IV. CONCLUSIONS

Overall, this research indicated that any of the three membranes studied is capable of successfully recycling the A-2000 P cleaner, as demonstrated by the high levels of surfactant passage through the three membranes. In particular, the results of this research indicate that for the Hayes Quench Oil, P Special Lard Oil, and Cutting Oil NC 205 test solutions, the use of ultrafiltration to extend the life of the cleaner bath could be viable. For these three test solutions, the retention of emulsified oils by the three different membranes is excellent and the passage of surfactant is high (assuming that high anionic surfactant passage indicates high passage of the other cleaner components through the membranes). The recovery of surfactant (and other cleaner components) is the key to a successful closed loop system and is what makes a UF system economically attractive and viable. However, the use of a closed loop UF system for situations where a semi-synthetic or totally synthetic contaminant (i.e., Coolex or Citcool 33) is present in the cleaning bath is not recommended based on this research. The flux curves generated for these test solutions were comparable to the curves generated for tap water, indicating that very little (if any) of the contaminants were retained by the UF membranes. Thus, it appears that the majority of the contaminant components pass through the membrane and will remain in the cleaning bath to be potentially redeposited on cleaned parts.

An additional conclusion drawn from this experimental work is that the PAN membrane does in fact appear to be more resistant to fouling and gel layer formation than ceramic and carbon membranes when oily contaminants are present in the cleaning solution. As stated, the PAN membrane is more hydrophilic than the Carbosep and

CFCC membranes, and actually repels oily contaminants. Whereas the Hayes Quench Oil, P Special Lard Oil, and Cutting Oil NC 205 test solution flux curves for the Carbosep and CFCC membranes quickly approached a limiting flux value (indicating rapid fouling and gel layer formation), the PAN membrane flux curves continued to increase across the entire range of transmembrane pressure drops. (However, this is not to say that the PAN membrane is superior to the other membranes in all situations when oily contaminants are present.). Also, this research demonstrates that the equations developed to describe flux and flux decline in UF are valid for this experimental work. The linear nature of the flux curves generated for tap water and the values of the empirical constant m calculated from the test solution flux decline versus time curves support the flux and flux decline equations presented in Sections 1.8 and 2.5, respectively.

Finally, this research verified a fact which was revealed during discussions with closed loop system manufacturers and vendors. This fact is that each cleaning application is very case specific and that the selection of a closed loop UF system for each application requires fairly extensive pilot testing. So many variables exist for any given cleaning application (e.g., cleaning solution temperature, type of aqueous cleaner, cleaning solution contaminants, etc.) that the development of "general" guidelines for UF system selection is very difficult. In addition, so many factors regarding UF system operation are variable (e.g., membrane type, transmembrane pressure, system feed flow rate, etc.) that multiple systems exist for any given cleaning application.

V. RECOMMENDATIONS FOR FUTURE WORK

Future work which should be performed to support the experimental work conducted for this study includes analyzing a permeate sample from each of the three membranes for a solution consisting of tap water and A-2000 P only. This would provide additional insight into the intrinsic recyclability of A-2000 P. A Chemical Oxygen Demand analysis of the A-2000 P solution before and after ultrafiltration would reveal the percentage of all cleaner components passing through the membranes, not just the percentage of anionic surfactant passage [Carmody, 1995].

Finally, a study comparing the performance of a cleaner of the same type as A-2000 P versus a fully-emulsifying cleaner would be interesting. As stated in Section 2.2, fully-emulsifying cleaners have been proven to perform well for closed loop applications, since they leave no "free" oils in the aqueous bath which could tend to rapidly foul non-hydrophilic membranes [Bernat, 1994]. These fully-emulsifying cleaners are capable of emulsifying on the order of ten times the amount of oils that a comparable amount of an A-2000 P-type cleaner could emulsify. In addition, fully-emulsifying cleaners hold their emulsions strongly over extended periods of time, whereas A-2000 P-type cleaners form weaker emulsions of a shorter duration [Bernat, 1996; Paul, 1996]. One proposed benefit of A-2000 P-type cleaners over fully-emulsifying cleaners is that more of the surfactants might pass through the UF membranes since they are not so strongly "tied up" in emulsions. A second proposed benefit is that the surfactants lost in the retained emulsified oils could be recovered after a short period of time when the emulsion breaks. For example, if the retentate from a closed loop UF system using an A-2000 P-type

cleaner is sent to a storage tank, the emulsion would (theoretically) break much more rapidly and easily (i.e., without additional treatment such as heat or chemical addition) than a retentate containing a fully-emulsifying cleaner. Once the emulsion breaks, the oil can be skimmed and the aqueous cleaning solution recycled. If the above assumptions regarding A-2000 P-type cleaners are true, a closed loop UF system using such a cleaner is economically and environmentally superior to an identical system using a fully-emulsifying cleaner. The system with the A-2000 P-type cleaner would recycle the cleaner more easily and generate a smaller volume of emulsified oil waste.

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Appendix A: A-2000 P Cleaner Literature

POLY CHEM

U.S. POLYCHEMICAL CORPORATION

EXECUTIVE OFFICES · PLANT · LABORATORY
P.O. Box 268 · Spring Valley, NY 10977

POLYCHEM A-2000 P

Description:

Polychem A-2000 P is a non-silicated, non-chelated, non-etch alkaline soak cleaner for removing mill oils, grease, buffing compounds, stencil marks, finger prints, stamping oils from steel, stainless steel, steel alloys, copper and its alloys, and aluminum and aluminum alloys.

Polychem A-2000 P has exceptional cleaning ability with a high degree of safety to aluminum. It is recommended for cleaning prior to chromating, anodizing, etching or other conversion coating such as phosphating.

Polychem A-2000 P can be used in ultrasonic tanks. All applications must be followed by a water rinse.

Properties:

Composition	: Blend of surfactants and phosphates
Form	: Clear liquid
Odor	: Bland/mild
Specific Gravity	: 1.050
Foaming tendency	: Medium-high
Diluent	: Water
Use concentration	: Normally used at 5-10 % by volume
Use temperature	: 130° - 150°F
pH at working concentrations	: 9.3 - 9.5 at 10% by volume

Application Procedure:

Clean the solution tank. Add water to the operating level of the tank and heat to about 120°F. Add sufficient amount of Polychem A-2000 P to make a working solution of 5-10% by volume. Mix well and heat the solution to the operating temperature of 130°-150°F and process cleaning. Higher temperatures up to 180°F (82°C) may be used to speed up the cleaning of steel or stainless steel.

Safety and Handling Precautions: Polychem A-2000 P is a mildly alkaline cleaner. Direct contact may cause irritation of the eyes and skin. Avoid prolonged contact with skin. Wash thoroughly after handling. Do not take internally.

POLY★CHEM

U.S. POLYCHEMICAL CORPORATION

EXECUTIVE OFFICES · PLANT · LABORATORY
P.O. Box 288 · Spring Valley, NY 10977

HMIS

Health	1
Fire	0
Reactivity	0
Personal Protection	B

MATERIAL SAFETY DATA SHEET

SECTION I – PRODUCT INFORMATION

MANUFACTURE'S NAME   U.S. POLYCHEMICAL CORP

STREET ADDRESS   584 CHESTNUT RIDGE ROAD

EMERGENCY TELEPHONE NO.   914-356-5530

INFORMATION TELEPHONE NO.

MANUFACTURE'S CODE IDENTIFICATION

PREPARATION DATE   NOVEMBER 22, 1995

CITY, STATE AND ZIP CODE   CHESTNUT RIDGE, NY 10977

PRODUCT CLASS   AQUEOUS ALKALINE CLEANER

TRADE NAME   POLYCHEM A-2000 P

SECTION II – HAZARDOUS INGREDIENTS

INGREDIENT	CAS NO	PERCENT	OCCUPATIONAL EXPOSURE LIMITS	
			TLV PPM	STEL PPM
TETRA POTASSIUM PYRO PHOSPHATE	7320-34-5	3 - 8	Not applicable	Not applicable

---

SECTION III – PHYSICAL DATA

BOILING RANGE   Approximately 212°F

VAPOR DENSITY   ( ) HEAVIER   ( ) LIGHTER THAN AIR   Not applicable

EVAPORATION RATE   ( ) FASTER   Not
( ) SLOWER THAN   Applicable
ETHER

PERCENT
VOLATILE   Above 70
BY VOLUME

WEIGHT
PER
GALLON   11 Lbs

SECTION IV – FIRE AND EXPLOSION HAZARD DATA

FLAMMABILITY CLASSIFICATION   OSHA   N/A   FLASH POINT   None   LEL Not Applicable
DOT

EXTINGUISHING MEDIA
(X) FOAM   (X) ALCOHOL FOAM   (x) CO2   (x) DRY CHEMICAL   (X) WATER FOG   ( ) OTHER

UNUSUAL FIRE AND EXPLOSION HAZARDS   None known

SPECIAL FIRE FIGHTING PROCEDURES   Not applicable

Outside NY State Call Toll Free (800) 431-2072   From NY State Call Collect (914) 356-5530

FAX #(914) 356 6656

Polychem A-2000 P

SECTION V — HEALTH AND HAZARD DATA

EFFECT OF OVER EXPOSURE   Irritation of skin and eyes. Defatting of skin.

MEDICAL CONDITIONS PRONE   Skin contact may aggravate an existing dermatitis
TO AGGRAVATION BY EXPOSURE

PRIMARY ROUTE(S) OF ENTRY   (x)   DERMAL   (x)   INHALATION   (x)   INGESTION

EMERGENCY AND FIRST AID PROCEDURES

    Eyes   Flush eyes with plenty of water, for 15 minutes. If irritation persists get medical attention.
    Skin: Wash skin with plenty of water. Wash clothing before reuse.
    Swallowing Drink several glasses of milk. Get medical attention.

SECTION VI — REACTIVITY DATA

STABILITY   ( ) UNSTABLE   (x) STABLE   CONDITIONS TO AVOID Do not mix with acids.

INCOMPATIBILITY (MATERIALS TO AVOID)   Acids, strong oxidizing agents.

HAZARDOUS DECOMPOSITION PRODUCTS   Burning of materials may produce oxides of carbon, nitrogen and phosphorus

HAZARDOUS POLYMERIZATION   ( ) MAY OCCUR   (x)   WILL NOT OCCUR

SECTION VII — SPILL OR LEAK PROCEDURES

STEPS TO BE TAKEN IN CASE MATERIAL IS RELEASED OR SPILLED   Collect on absorbent material. Rinse area with plenty of water

WASTE DISPOSAL METHOD   Dispose in accordance with Federal, State and Local Regulations.

SECTION VIII — SPECIAL PROTECTION INFORMATION

RESPIRATORY PROTECTION   None normally required

VENTILATION   General room ventilation.

PROTECTIVE GLOVES   Gloves
EYE PROTECTION   Goggles   OTHER PROTECTIVE EQUIPMENT   Eye wash station

SECTION IX — SPECIAL PRECAUTIONS

PRECAUTIONS TO BE TAKEN IN HANDLING AND STORAGE   Store in cool dry place.

OTHER PRECAUTIONS   Avoid prolonged contact with skin.

THIS INFORMATION IS OFFERED IN COMPLIANCE WITH OSHA REQUIREMENTS BASED ON AVAILABLE DATA. WE BELIEVE THE
INFORMATION IS ACCURATE. SUBMISSION OF THIS INFORMATION DOES NOT CONSTITUTE ANY WARRANTY EITHER STATED OR
IMPLIED. USER ASSUMES ALL LIABILITY FOR PROPERLY USING THIS INFORMATION.

Appendix B: Contaminant Compositions

The following table lists the five contaminants and their respective components used in the test solutions for this experimental study. Note that the components listed for each contaminant include only those that were listed by the manufacturer. Many of the contaminants contain proprietary, unidentified components.

Contaminant Manufacturer and Name	Component Name	Component Molecular Weight
Park Chemical Company: Hayes Quench Oil	Mineral Oils	250 to 300
W.A. Wood Company: P Special Lard Oil	Petroleum Lubricating Oil Base Stock	250-300 250-300
Citgo Petroleum Inc.: Cutting Oil NC 205	Refined Petroleum Oils Triethanolamine	250-300 149
Cooks Industrials Lubricants: Coolex 40	Petroleum Based Oils Hexylene Glycol Polyethylene Glycol Dioleate Triethanolamine Oleate	250-300 128 590 430
Citgo Petroleum Inc.: Citcool 33	Monoethanolamine Diethanolamine Triethanolamine Sebacic Acid	61 115 149 202